Chemical attack of strong chloride solutions on concrete. Does experience confirm that different chloride salts may influence concrete in different ways?

Peterson, Olof

1984

AVDELNINGEN FÖR BYGGNADSMATERIALLÄRA
LUNDS TEKNISKA HÖGSKOLA
DIVISION OF BUILDING MATERIALS
LUND INSTITUTE OF TECHNOLOGY
Box 118
S-221 00 LUND

CHEMICAL ATTACK OF STRONG CHLORIDE SOLUTIONS ON CONCRETE

Olof Peterson

Does EXPERIENCE confirm that different chloride salts may influence CONCRETE in different ways ?

JULY, 1984

RAPPORT TVBM-3020
LUND SWEDEN

CODEN: LUTVDG/(TVBM-3020)/1-30/(1984)

ISSN 0348-7911

CHEMICAL ATTACK OF STRONG CHLORIDE SOLUTIONS ON CONCRETE

Olof Peterson

Does EXPERIENCE confirm that different chloride salts may influence CONCRETE in different ways ?

JULY, 1984

RAPPORT TVBM-3020
LUND SWEDEN

CONTENTS

PREFACE

Certainly, damage to concrete is known, which is caused by chlorides secondarily.

Even in low concentration, a chloride solution promotes the corrosion of steel in concrete, e. g. reinforcement.

Deicing with chlorides, but also with any other water soluble deicing agents, often cause loss of material from concrete surfaces.

Concrete or porous stone in a structure, founded where the ground water is saline, runs the risk to be damaged when the water rises in the pore system by capillarity to a level above the surface of the ground. When water evaporates, the pore water grows saturated, and salts may cristallize. Under special conditions, the crystallizing salts may damage the porous concrete, or stone. The salts need not necessarily be constituted of chlorides.

Bonzel and Locher stated (1968) that the chloride content of a solution does not attack concrete. Certainly, they knew that solutions of magnesium chloride or ammonium chloride may dissolve parts of the cement paste, and they regarded the attack as one of magesium ions or ammonium ions, not of chloride ions.

In the literature from the most recent decades, cases are reported, which indicate that the chloride ion may play an important rôle of itself.

The purpose of this paper is to put together what is known, and what is only believed, about the chemistry of chloride attack on cement paste.

The first chapter contains observations, described in the literature.

The second chapter contains a discussion, from chemical and physical point of view, of what should be concluded from the observations in the first chapter.

I should appreciate very much, if you, Dear Reader, would please to communicate to me, or to Professor Arne Hillerborg, any experience that points to the possibility that damage to concrete is caused by chlorides in a way, which is not covered up in this short study.

SUMMARY

Strong solutions of magnesium chloride, calcium chloride, and sodium (or potassium) chloride influence concrete or mortar in different ways.

For magnesium chloride and calcium chloride, the concentration has a great importance. If the concentration is high, the solid calcium hydroxide in the cement paste suffers a conversion to chloro-hydroxide hydrates, and those may rapidly damage the concrete. The damage can not be prevented by keeping the water cement ratio low.

For calcium chloride, the temperature is important, and the damage does not take place in the temperature range 35 - 50 degrees C.

Slag cement with a slag content above 70 percent does not form much calcium hydroxide during the hardening and curing processes. Concrete with such cement is not damaged by strong magnesium or calcium chloride solutions. Still, the gain in strength is somewhat reduced, compared with the results on storing in pure water.

Sodium or potassium chloride solutions do not convert solid calcium hydroxide to chloro-hydroxide hydrate, and such salt solutions do not damage concrete. For Portland cement concrete, the gain in strength is somewhat reduced, but not for slag cement concrete, compared with the same types of concrete stored in pure water.

Portland cement concrete, on storing in strong solutions of sodium or potassium chloride, forms sodium or potassium hydroxide, enough to cause alkali-silica reactions if the aggregate contains alkali sensitive types of minerals.

It is claimed that sodium or potassium chloride solutions, and also magnesium or calcium chloride solutions in such a low concentration that the expansive chloro-hydroxide hydrates do not form, are able to cause a loss of solid calcium hydroxide from the hardened cement paste, when the chloride ions penetrate the concrete. This will increase the porosity and reduce the strength of the concrete.

The explanation is given that the chloride ions penetrate concrete more rapidly than the metal ions. The electric charge of the concrete must be kept constant, and this condition is fulfilled through an amount of hydroxide ions leaving the cement paste, corresponding to the chloride ion excess. This excess is greater for magnesium chloride than for potassium chloride.

If this theory is correct, even sodium chloride should be capable to cause a loss of calcium hydroxide in the cement paste, when the salt penetrates concrete. It would be of great interest if it could be stated, whether the theory is correct or not.

1. EXPERIENCE OF CHLORIDE ATTACKS ON CONCRETE

Calleja (1980) quotes from Ushiyama and Goto (1974) and tries to explain the capacity of chlorides to dissolve solid calcium hydroxide with "mutual diffusion" or "counter-diffusion" of Cl^- ions and OH^- ions. The explanations by Ushiyama and Goto are:

1. When concrete is stored in a chloride solution, chloride ions diffuse into concrete, and the diffusion speed is dependent of the salt, in which the chloride is a part. The chloride ions of magnesium chloride diffuse most rapidly, and the diffusion speed decreases in the order:

   $MgCl_2 > CaCl_2 > LiCl > KCl > NaCl$

2. In all those salts, the chloride ions diffuse much more rapidly than the metal ions:

   $Cl^- >> K^+ > Na^+ > Li^+$

3. This difference in diffusion speed has the immediate consequence that more chloride ions than metal ions penetrate the hardened cement paste. According to the "mutual diffusion theory", the paste will lose an amount of hydroxide ions, OH^-, corresponding to how much the amount of chloride ions exceeds the equivalent amount of corresponding metal ions.

   Thus, most hydroxide ions should be lost if the concrete is stored in magnesium chloride, and the difference, for some salts, decreases in the order:

   $MgCl_2 > CaCl_2 > LiCl > NaCl > KCl$

This mechanism could explain the loss of calcium hydroxide in concrete, stored in a strong chloride solution.

However, the presumption that the solid calcium hydroxide always becomes "washed" out from the concrete, may be true in the case of a dilute magnesium chloride solution, but not necessarily in the case of a strong calcium chloride solution.

Furthermore, the theory does not explain why expansion may occur, when some chloride solutions penetrate concrete or cement mortar, especially at a temperature of 25 degrees C or lower, but above the freezing point.

For the diffusion measurements, a cement paste plate was used, 0.3 cm thick. It is very probable that the porosity of this plate may change during the test as a result of chemical reactions.

Wannerberg (1982) has studied concrete that has become impregnated with chlorides and then has mouldered. He has expressed the chloride content as $CaCl_2$, calculated in percent of the cement weight of the concrete. His experience was that concrete is likely to remain permanent, if the percentage is below 0.2. Serious damage is to expext (or does already exist) if the percentage is above 0.5 percent.

Wannerberg believed that concrete, manufactured according to modern knowledge and with good air entraining agents and the water cement ratio of which does not exceed 0.5, probably will resist an essentially higher chloride percentage.

It is not known, which of the metals magnesium, calcium, sodium or potassium has been the counter ion to the chloride analyzed. Most probable the counter ion has been sodium. Nor is it known, whether the damage has been caused by chemical reactions, or crystallization of concentrated chloride solutions.

In Chapter 2, the chemical reactions are to be treated, which are plausible in a cement paste in contact with chloride solutions, especially strong solutions.

1.1 Magnesium chloride attacks

Smolczyk (1968) described the attacks on model mortars of magnesium chloride solutions with a concentration of 3 mol/l.

No damage could be observed on mortars with blastfurnace slag cement with 75 % slag, either the water cement ratio was 0.5 or 0.7, and even after 1.5 years of storing.

Mortars with Portland cement were severely damaged within 16 weeks.

The calculated content of tricalcium aluminate, C_3A, only insignificantly influenced the time when the first crack was observed.

C in C_3A stands for CaO (calcium oxide), and
A for Al_2O_3 (aluminium oxide).

A low water cement ratio (0.5) did not necessarily make the mortar more resistant to damage than a moderate one (0.7).

After two years storing in magnesium chloride solution, the strength of the Portland cement mortar test cubes was lost, or almost lost.

The strength of the slag cement mortar test cubes was reduced to
about 70 percent with water cement ratio 0.5, and to
about 45 percent with water cement ratio 0.7,
in relation to the correspondent test specimens stored in water.

X-ray diagrams of mortar, the Portland cement of which contained 12 % C_3A, show that the main crystalline reaction product was the phase

(1) $MgO.MgCl(OH).5H_2O$

dimagnesium monochloro-hydroxide hydrate

Its formation from calcium hydroxide is accompanied with a volume expansion, which can be calculated to a factor of two. (Chapter 2.1)

No portlandite (calcium hydroxide, $Ca(OH)_2$) could be detected. This observation seems spectacular, because the phase is very easy to recognize in an X-ray diagram after normal hydration of a Portland cement mortar.

X-ray diagrams of slag cement mortar show no sign of the phase (1) above, but moderate amounts of the phase

(2) $3CaO.(Al,Fe)_2O_3.CaCl_2.10H_2O$

calcium chloro-(aluminate, ferrite) hydrate

This phase is called, in German, "Friedel'sches Salz".

It may be a natural question, why attack of magnesium chloride shapes a new phase with calcium chloride as a component. This will be explained in the sub-chapter 2.1.

No portlandite is detected. In a slag cement mortar, however, this phase is essentially less abundant than in a Portland cement mortar, even after curing in pure water.

Moderate amounts of gypsum, $CaSO_4.2H_2O$, are indicated.

Suzukawa (1980) described testing of mortars with four types of Portland cement, one type of blast-furnace slag cement, and one type of fly-ash cement. The specimens were cured for only one week before the magnesium chloride solution test.

The concentration of the test solution was 1, 4, and 25 g $MgCl_2$/l, which corresponds to 0.01, 0.04, and 0.26 mol/l. It is to be observed that Suzukawa's work was performed with much more dilute test solutions (at least 10 times) than Smolczyk's. As a comparison, the North Sea (at Helgoland) contains 0.55 mol Mg^{2+}/l.

The water cement ratio was 0.65. In spite of the low concentration of the test solution, the compressive strength of the Portland cement mortar specimens after 52 weeks storing in the 0.26 mol/l solution was reduced to 50-60 percent of the value for mortar stored in pure water.

The specimens with Portland blast-furnace slag cement maintained 94 percent of their compressive strength after water storing.

The surfaces of the specimens were covered with a white film, consisting mainly of magnesium hydroxide, $Mg(OH)_2$. Formation of a magnesium hydroxide film was described already by Kalousek and Benton (1970).

The author refers to Riedel (1973) about another phase, magnesium oxychloride

(3) $Mg_2Cl(OH)_3 \cdot 4H_2O$

dimagnesium monochloro-hydroxide hydrate

The phase is chemically identical with the phase (1), and a condition for its formation is a high concentration of magnesium chloride in the solution. 25 g/l is a too low concentration for formation of (1) or (3).

The loss of calcium hydroxide in the hardened cement paste probably explains why the compressive strength gradually decreases after a long time of storing in the solution.

Since the magnesium hydroxide forms only at the surfaces of the test specimens, no expansion of the specimens is to be feared.

1.2 Calcium chloride attacks

Smolczyk (1968) described the action on model mortars of calcium chloride solutions with a concentration of 3 mol/l.

Mortars with blastfurnace slag cement with 75 % slag did not change even after 1.5 years, neither with a water cement ratio of 0.5 nor 0.7.

Mortars with Portland cement were damaged, or had at least cracked heavily, within 16 weeks.

The calculated content of tricalcium aluminate, C_3A, only insignificantly influenced the time when the first crack was observed; the influence of the water cement ratio seems to be greater.

C in C_3A stands for CaO (calcium oxide), and
A for Al_2O_3 (aluminium oxide).

No strength values were given, since the test cubes had not still been stored for two years in calcium chloride solution, when this paper by Smolczyk was published.

X-ray analyses of mortar, the Portland cement of which contained 12 % C_3A, showed that the main mineral was

(4) $CaO.CaCl_2.2H_2O$

dicalcium dichloro-hydroxide hydrate

The formation of this phase from calcium hydroxide is accompanied with a volume expansion, which can be calculated to a factor of at least three.

No portlandit (calcium hydroxide, $Ca(OH)_2$) could be detected.
After normal hydration of a Portland cement mortar, the calcium hydroxide phase is always easy to recognize.

Small amounts of

(2) $3CaO.(Al,Fe)_2O_3.CaCl_2.10H_2O$

calcium chloro-(aluminate, ferrite) hydrate

was also detected.

X-ray analyses of mortar with slag cement indicated small amounts of gypsum, $CaSO_4.2H_2O$.

No portlandite (calcium hydroxide) was indicated. The content of this mineral was small also after storing in pure water.

Small amounts of the phase "mono-sulphate":

(5) $3CaO.(Al,Fe)_2O_3.(CaO,CaSO_4).aq$

calcium (monosulphate, hydroxide)-(aluminate, ferrite) hydrate

are indicated. This phase also occurs after storing slag cement mortar in pure water.

Chatterji and Damgaard Jensen (1975) refer to sources, which state that neither thermal shock nor osmotic pressure is a necessary condition for the calcium chloride attack on concrete at any temperature above the freezing point.

The difference between the strong attack from a concentrated calcium chloride solution, and the essentially weaker attack from a sodium chloride solution can not be explained by the formation of chloroaluminate complexes, since such phases form at the attacks of both types of salt solutions.

Chatterji and Damgaard Jensen treated concrete specimens with 30 percent calcium chloride solutions at 5, 20, and 40 degrees C. Their results indicated that:

1. The salt solution must penetrate the surface layers of the concrete. According to the physical laws, it is probable that the ions penetrate more rapidly, the higher the temperature is.

2. At 40 degrees C, no cracks were formed within 3 months, even if the concentration of the calcium chloride solution was increased to 60 weight percent.

3. At 20 degrees C, the first crack was visible after 34 days. If the specimen was stored at 40 degrees C during the first 14 days, then the first crack appeared already after 28 days.

   This difference of 6 days <u>may</u> be due to the more rapid penetration of the calcium chloride solution during the 40 degrees period.

4. At 5 degrees C, the first crack was visible after 20 days. If the specimen was stored at 40 degrees C during the first 14 days, then the first crack appeared already after 16 days.

   This difference of 4 days may be due to the more rapid penetration of the calcium chloride solution during the 40 degrees period.

Generally, the expansion comes more rapidly after storing at 5 degrees than at 20 degrees.

Probably, the calcium chloride solution penetrates the concrete more rapidly at 40 degrees than at 20 or 5 degrees C.

Nielsen and Krogh (1976) stored mortar prisms in 10 weight percent calcium chloride solution (about 1.0 mol/l) at 5 and 25 degrees C, and in 30 weight percent solution (about 3.4 mol $CaCl_2$/l) at 5, 25, 35, and 50 degrees C.

The prisms in the stronger solution at 5 and 25 degrees C lost material along their edges within three days. Within 8 days several cracks appeared, and the prisms were totaly destroyed within 11 days.

The prisms in the same strong solution, stored at 35 and 50 degrees C, showed no visual signs of destruction, but their resonance frequency in flexural swinging mode were notably decreased.

The prisms in the weaker solution did not show any other change than a notable decrease in resonance frequency, even when stored at the more dangerous temperatures 5 and 25 degrees C.

X-ray analyses showed that the portlandite (calcium hydroxide) content of the hardened Portland cement mortar was less after storing in 10 percent calcium chloride solution than after storing in pure water.
The decrease was greatest after storing at 5 degrees C.

After storing in 30 percent calcium chloride solution no portlandite could be detected at all.

No new minerals could be detected in the mortar after storing in 10 percent calcium chloride solution.

After storing in 30 percent calcium chloride solution, the new phase

(6) $C_3A.CaCl_2.10H_2O$

calcium chloro-aluminate hydrate

C stands for CaO (calcium oxide)

A stands for Al_2O_3 (aluminium oxide)

was detected. The phase could possibly be identical with phase (2), which also may contain some ferric iron, Fe^{3+}.

When the storing temperature was 5 or 25 degrees C, the mortar also contained the phase

(4) $CaO.CaCl_2.2H_2O$

dicalcium dichloro-hydroxide hydrate

Test prisms with this phase desintegrated rapidly, and the authors conclude that the phase may have caused the break down. They are, in this respect, not in opposition to Smolczyk, who claimed that there occurred an expansion (calculated by me to a factor of three) when the phase is formed from solid calcium hydroxide.

1.3 Sodium chloride attacks

Smolczyk (1968) described tests with saturated solutions of sodium chloride (about 5.4 mol/l) on model mortars.

No visible attack on the mortar cubes could be noted after two years, but the compressive strength of Portland cement mortar was reduced to about 60 percent of the strength after storing in pure water.

Mortar with blastfurnace slag cement with 75 % slag had not lost very much strength, compared with that of the same type of mortar, stored for the same time (2 years) in water.

X-ray analyses of mortar, the Portland cement of which contained 12 % C_3A, indicated contents of crystals of sodium chloride.

The amounts of the phase

(2) $3CaO.(Al,Fe)_2O_3.CaCl_2.10H_2O$

calcium chloro-(aluminate, ferrite) hydrate

were essentially larger after storing in saturated sodium chloride solution than after storing in calcium chloride solution (3 mol/l).

Portlandite (calcium hydroxide, $Ca(OH)_2$) was detected in amounts, equal to those detected after storing in pure water.

X-ray analyses of slag cement mortar indicated the same types of new minerals as did the analyses of Portland cement mortar, but the content of portlandite was reduced to about 30 percent of the one after storing in pure water. The level is essentially lower than in Portland cement mortar.

Jespersen and Krogh (1976) tested storing of Portland cement mortar in sodium chloride solutions with concentrations of 10 and 17.5 weight percent, and saturated solution (about 26.5 weight percent). The chloride concentrations correspond to 1.8, 3.4, and 5.4 mol/l.

Some of the specimens contained non-reactive aggregate, and others alkali-reactive aggregate.

The prisms were stored at 25 and 50 degrees C.

After storing at 50 degrees C, mortar prisms with reactive aggregate have shown gel flow, pop-outs and cracks.

After storing at 25 degrees C, such mortar prisms have shown gel flow with 17.5 weight per cent sodium chloride and also with saturated solutions.

Examination with scanning electron microscope have shown gel, and also loss of calcium hydroxide, in test prisms with reactive aggregate.

Midgley and Illston (1980) described an investigation of the penetration of chloride ions into hardened Portland cement pastes, with water cement ratios of 0.23, 0.47, and 0.71.

They used sodium chloride solutions with the concentration 30 g/l (0.51 mol/l), chosen because of its similarity of sea water, and 150 g/l (2.57 mol/l), which corresponds to 5 times the concentration of sea water.

The penetration was described in the Table 1 below.

Table 1

Penetration of chloride ions into hcp at 6 months.

$c = kd^{-m}$
c = concentration of chloride ion wt%
d = distance into hcp in mm
k = constant reflecting depths of penetration
m = slope of relationship $mc = k' + m.\ln d$
r = correlation coefficient of linear regression.

Mark	k	m	r	Chloride wt% in bottom 14mm	Chloride wt% in top 14mm
0.23/s	17.3	-0.08	0.82	0.00	0.26
0.23/5s	22.4	-0.10	0.73	0.00	0.46
0.47/s	27.6	-0.68	0.99	0.03	0.55
0.47/5s	27.6	-0.42	0.85	0.02	0.90
0.71/s	27.6	-0.75	0.85	0.10	1.13
0.71/5s	27.6	-0.65	0.83	0.14	2.43

The penetration increased with increased value of the water cement ratio.

Chemically, the chloride ions may form the calcium chloro-aluminate

(7) $3CaO.Al_2O_3.CaCl_2.12H_2O$

calcium chloro-aluminate hydrate

which, according to the authors, is deleterious for the concrete. In spite of the higher content of water, the phase might be identical with the phase (2) and (6) with 10 H_2O.

Quantitative X-ray diffraction analysis showed that a considerable amount of chloride is not locked up in the crystalline phase (6). Instead, it may be present as free chloride ions in the fine capillaries, or it may be built into the calcium silicate hydrate lattice, which could be shown only for paste with the water cement ratio 0.71. According to the authors, it is benificial for the concrete that chloride ions are built into the calcium silicate hydrate lattice.

The X-ray analyses did not show any change in the content of other crystalline phases in the hardened cement pastes, such as calcium hydroxide, calcium aluminate hydrates, or calcium sulphoaluminate hydrates. So, the authors claim, the phase (6) must be formed from anhydrous calcium aluminate in unhydrated clinker particles.

2. DISCUSSION

In this Chapter, the observations from the Chapter 1. are used for getting a picture, in chemical respect, of what happens to the concrete when stored in one of the three chloride solutions.

The contents of the Chapter 1. show that this picture is different for the three counter ions magnesium, calcium, and sodium. Thus the discussion has to be performed independently for each of the three salts.

2.1 Magnesium chloride

Common for all experience of magnesium chloride attack on concrete with Portland cement is that the cement paste loses all, or most of, its content of solid calcium hydroxide. Thus, the concrete or mortar grows more porous, and eventually loses part of its strength.

For explaining why a magnesium salt solution, e. g. magnesium chloride, is able to dissolve solid calcium hydroxide, it is sometimes asserted that magnesium hydroxide is a weaker base than calcium hydroxide.

There really is a small difference in strength between the two bases, but more essential is that the solid magnesium hydroxide is less soluble in water than solid calcium hydroxide.

In pure water, calcium hydroxide dissolves, until the calcium ion concentration is about 0.02 mol/l, and the corresponding hydroxide ion concentration equals 0.04 mol/l.

This means that the pH value of the water will rise, until it reaches

(8) $$pH = 14 + \log 0.04$$

$$pH = 12.6$$

If the pH value is at least so high, the water is saturated, and no more calcium hydroxide dissolves.

Solid magnesium hydroxide is far less soluble in pure water: the ion concentrations in a saturated solution will approach 1.54×10^{-4} mol/l for magnesium ions, and 3.09×10^{-4} mol/l for hydroxide ions.

In this solution, the pH value would reach

(9) $$pH = 14 + \log 3.09 \times 10^{-4}$$

$$pH = 10.5$$

In a dilute magnesium chloride solution, e. g. 0.26 mol/l, the solid magnesium hydroxide certainly will give a still lower pH value.

If Portland cement concrete is immersed in a dilute solution of magnesium chloride, hydroxide ions start to diffuse into the solution from crystals of solid calcium hydroxide. As soon as the pH value approaches 10.5, magnesium hydroxide starts to precipitate. Thus, the pH value can not exceed the value 10.5 before most of the magnesium ions are consumed. At this low initial concentration of the magnesium chloride solution, principally all the magnesium will be precipitated as a slimy skin of magnesium hydroxide on the surface of the concrete, and hardly any magnesium ions will enter the pore system of the concrete.

By this mechanism, a difference is maintained between the hydroxide ion concentration in the solution and the one at the surface of a calcium hydroxide crystal in the surface layer of the concrete. The difference will promote a lasting diffusion of hydroxide ions from the surface of the calcium hydroxide crystal into the magnesium chloride solution. The concentration of hydroxide ions at the surface of the calcium hydroxide crystal is maintained by a lasting dissolution of calcium and hydroxide ions from the surface of the crystal.

In the same time, there is a difference of concentration of chloride ions between the solution, e. g. 0.52 mol/l, and the interior of the concrete, where the concentration, initially, is near to zero. This difference is far greater than the difference in hydroxide ions. However, since the positively charged magnesium ions cannot penetrate the concrete surface, the two currents of negatively charged ions will balance each other.

Hydroxide ions will leave the concrete, and an equivalent amount of chloride ions will enter the concrete.

Thus, the surface layer of the concrete will contain a solution of calcium chloride. Probably, the concentration in mol/l of this calcium chloride solution will approach, but not reach, the end concentration of the magnesium chloride bath.

The strength of the concrete will gradually decrease, but no cracks or other visible damage will occur.

If the magnesium chloride solution is made stronger, a limit will be reached, above which another mechanism of attack will set in.

In a water solution of magnesium chloride, the magnesium ions never occur sole. In a dilute water solution, the magnesium ion normally is surrounded by six water molecules as a complex ion:

(10) $$Mg^{2+} + 6H_2O = \left[\begin{array}{ccc} & H_2O & \\ H_2O & Mg^{2+} & H_2O \\ H_2O & & H_2O \\ & H_2O & \end{array}\right]^{2+}$$

In a more concentrated solution, the probability increases for one of the water molecules to be substituted with a chloride ion:

(11) $$\left[\begin{array}{ccc} & H_2O & \\ H_2O & Mg^{2+} & H_2O \\ H_2O & & H_2O \\ & H_2O & \end{array}\right]^{2+} + Cl^- =$$

$$= \left[\begin{array}{ccc} & Cl^- & \\ H_2O & Mg^{2+} & H_2O \\ H_2O & & H_2O \\ & H_2O & \end{array}\right]^{+} + H_2O$$

When such chloro-pentaquo-magnesium ions occur frequently, the probability decreases for precipitation of pure magnesium hydroxide. Instead, a magnesium chloro-hydroxide forms. Such a compound is well known in connection with, what is known as "Sorel cement". A 20 percent solution of magnesium chloride is mixed with a special quality of magnesium oxide, and a solid phase,

(12) $3MgO.MgCl_2.11H_2O$

is formed, serving as the cementing agent in the hardened Sorel cement. This phase seems to be chemically identical with the one reported by Smolczyk (1968) and Riedel (1973).

When a magnesium chloride solution with a concentration of 3 mol/l surrounds a piece of Portland cement concrete, the solution penetrates the surface of the concrete, and a chloro-hydroxide phase (1) or (3) forms in the pore system:

(1) $MgO.MgCl(OH).5H_2O$

or rather

(3) $Mg_2Cl(OH)_3.4H_2O$

Those phases are chemically identical with the phase (12) above.

The following chemical reaction may be assumed:

(13) $$3Ca(OH)_2 + 4Mg^{2+} + 8Cl^- + 8H_2O =$$
$$= 2Mg_2Cl(OH)_3.4H_2O + 3Ca^{2+} + 6Cl^-$$

The calcium hydroxide has the formula weight 3 x 74.09 = 222.27, and the corresponding "formula volume" is 222.27/2.24 = 99.2.

The dimagnesium monochloro-hydroxide hydrate has the formula weight 2 x 207.16 = 414.3. Assumed that its density approaches the value 2 g/cm^3, the formula volume of the phase is 413.3/2 = 207.

This means that the new phase takes a space with about double the one of the calcium hydroxide consumed, and this fact may explain why concrete with the dimagnesium monochloro-hydroxide phase eventually becomes damaged, or at least cracks.

It is often recommended to mix a concrete with a low water cement ratio, e. g. 0.5, in order to increase the resistance of the concrete to attack from aggressive solutions. According to Smolczyk (1968), cracks may develop no later in a low ratio (0.5) concrete than in a plain concrete with the water cement ratio equal to 0.7

The paste with a high water cement ratio gives the concrete a low tensile strength, but the larger volume of capillary pores allows more of the new phase to form, before a dangerous pressure can build up and form cracks.

The calcium chloride solution, formed according to the reaction (13), explains why the calcium chloro-aluminate hydrate (2) can be formed in concrete during storing in magnesium chloride solution.

2.2 Calcium chloride

In all papers about the attacks on concrete of calcium chloride solutions, rather strong solutions are treated.

Characteristic for the attack of calcium chloride solutions on Portland cement concrete is that the portlandite, or calcium hydroxide, phase in the hardened cement paste was diminished in 1 mol/l solution, and disappeared in 3 mol/l solution of calcium chloride. This was true for all temperatures from 5 to 50 degrees C.

At temperatures from 5 to 25 degrees, and at a concentration of 3 mol/l, the concrete cracked, and eventually was totally damaged.

The calcium hydroxide may disappear by

1. Dissolution in the calcium chloride solution

2. Transformation of the calcium hydroxide to another phase

3. Calcium hydroxide may be used up in a chemical reaction

2.2.1 Solubility of calcium hydroxide in calcium chloride solution

Calculated from the solubility product of calcium hydroxide, 32×10^{-6} $(mol/l)^3$, the hydroxide ion concentration in a saturated calcium hydroxide solution, the calcium chloride concentration of which is 3 mol/l, should be equal to

$$(14) \qquad (32 \times 10^{-6}/3.0)^{0.5} = 3.27 \times 10^{-3} \text{ mol/l}$$

It is to be suspected that the chloride ions in a calcium chloride solution are able to form complex ions with calcium ions in a way, similar to the one discussed for strong magnesium chloride solutions (11). Thus, the law of solubility product may be brought, more or less, out of power.

Atherton Seidel (1940) shows in some tables that the solubility of calcium hydroxide does not decrease, according to (14), when calcium chloride is added to the calcium hydroxide solution, but increases when the addition is moderate. Even in very strong solutions av calcium chloride, the calcium from dissolved calcium hydroxide never exceeds 0.045 mol/l, compared with about 0.02 mol/l in pure water.

Thus, the increased solubility of calcium from solid calcium hydroxide can not explain why the calcium hydroxide phase disappears from hardened Portland cement paste, immersed in calcium chloride solution.

2.2.2 Transformation of the calcium hydroxide to another phase

An interesting observation in the tables of Seidel (1940) is that the solid calcium hydroxide remains the stable solid phase in contact with a calcium chloride solution, only if the concentration of calcium chloride is less than 1.88 mol/l.

Calcium ions in a water solution mainly occurs in hydrated state, like magnesium ions (10). If the chloride ion concentration is high enough, a chloro-complex ion, similar to (11), is to be expected.

Thus, according to Seidel, within the range from 1.88 mol/l to 33.72 weight percent $CaCl_2$, calcium hydroxide is not stable as a solid phase, but a chloro-hydroxide

(15) $4CaO.CaCl_2.14H_2O$

or rather

$Ca_5Cl_2(OH)_8.10H_2O$

pentacalcium dichloro-hydroxide decahydrate

When the calcium chloride solution is still more concentrated, above 33.72 weight percent $CaCl_2$, another chloro-hydroxide with higher content of chloride turns to be the stable solid phase:

(4) $CaO.CaCl_2.2H_2O$

or rather

$Ca_2Cl_2(OH)_2.H_2O$

dicalcium dichloro-hydroxide hydrate

This phase is identical with the one, found by Smolczyk (1968) in cement paste, immersed in a calcium chloride solution with a concentration of 3.0 mol/l.

The phase was also found by Nielsen and Krogh (1976) after storing Portland cement mortar at 5 and 25 degrees C in 30 percent calcium chloride solution. They could not detect the phase if the storing temperature was 35 or 50 degrees C.

An interesting question is: what happened to the calcium hydroxide crystals at those elevated temperature values?

2.2.3 Calcium hydroxide may be used up in chemical reactions

After storing Portland cement concrete in a strong solution of calcium chloride at any temperature between 5 and 50 degrees C, the "Friedel´sches Salz"

(2) $3CaO.(Al, Fe)_2O_3.CaCl_2.10H_2O$

(6) Al_2

(7) Al_2 $12H_2O$

with some of the formulations, given above, is recognized in X-ray diffraction analyses.

Since most of the tricalcium aluminate of the cement was consumed by the gypsum already at the hardening and curing of the concrete, the chloro-aluminates must be formed mainly by attack on the tetracalcium aluminate ferrite phase of the cement:

(16) $$C_4AF + 2Ca(OH)_2 + 2Ca^{2+} + 4Cl^- + 22H_2O =$$

$$= C_3A.CaCl_2.12H_2O + C_3F.CaCl_2.12H_2O$$

F stands for Fe_2O_3 (ferric oxide, iron(3)oxide)

Since the tetracalcium aluminate ferrite, C_4AF, contains only two molecules of calcium oxide for each molecule of aluminium or ferric oxide, calcium hydroxide is consumed at the attack by calcium chloride on this phase, but not at an attack on tricalcium aluminate.

According to (16) above, each gram of C_4AF consumes 0.3 g of calcium hydroxide. As a content of 10 weight percent of C_4AF is rather common for a Portland cement, this chemical reaction is not likely to be responsible for an important part of the total loss of calcium hydroxide.

Probably, those complex aluminate and ferrite salts are innocent of that crack formation in the concrete, which was observed by Nielsen and Krogh (1976) after storing in calcium chloride solution at 5 or 25 degrees C.

As stated in Chapter 1., Ushiyama and Goto (1974) proposed that hydroxide ions could be withdrawn from solid calcium hydroxide by "mutual diffusion" because the chloride ions diffuse much more rapidly into the cement paste than the calcium ions. Probably, the importance of this possible hydroxide loss is limited, but it may be combined with the formation of the calcium chloro-aluminate phase (16), because this reaction consumes chloride ions. The "mutual diffusion" theory could explain the loss of strength in mortar specimens, which is not combined with crack formation or other visible damage.

2.3 Sodium chloride

The nature of the attack seems to be different, when caused by sodium chloride solution, compared with the attacks of magnesium or calcium chloride solutions.

According to Smolczyk (1968), sodium chloride forms somewhat more of the calcium chloro-aluminate hydrate than calcium chloride does.

Probably, also for attack of sodium chloride solutions, the tetracalcium aluminate ferrite is attacked rather than the tricalcium aluminate, because the latter compound was consumed in a large extent by the gypsum at the hardening and curing of the concrete. The reaction must be somewhat different from the reaction (16):

(17) $$C_4AF + 4Ca(OH)_2 + 4Na^+ + 4Cl^- + 22H_2O =$$

$$= C_3A.CaCl_2.12H_2O + C_3F.CaCl_2.12H_2O + 4Na^+ + 4OH^-$$

F stands for Fe_2O_3 (ferric oxide, iron(3)oxide)

This reaction will consume twice as much calcium hydroxide as the corresponding reaction with calcium chloride solution, because calcium must be supplied for the $CaCl_2$ groups, and not only for the two deficient calcium oxide groups in the C_4AF.

Provided that the cement contains 10 percent of C_4AF, the amount of calcium hydroxide, potentially consumable by reaction (17), might be 6 percent of the cement weight.

Reaction (17) is important as a source for sodium hydroxide:

(18) $0.3 \times 0.1 \times 1000 \times 2/(74.09 \times (0.5 - 0.15) = 2.3$ mol/l

It is assumed that the water cement ratio was 0.5, and that water corresponding to a fraction of 0.15 of the cement weight becomes bound in the hardening processes.

This potential sodium hydroxide source is much more important for alkali-silica reactions than the clinker alkalies ever can be.

2.3 mol/l would correspond to a pH value of:

(19) $pH = 14 + \log 2.3$

$pH = 14.36$

Alkali-silica reactions, provoked by strong solutions of sodium chloride, were reported by Jespersen and Krogh (1976). This principle is proposed for testing the resistance of concrete aggregates to alkali-silica reactions by immersing test specimens of cement mortar in a saturated sodium chloride solution.

Chatterji (1979) found that alkali silica reactions, provoked by sodium chloride treatment, could be prevented if the cement mortar specimens were stored for 4 weeks in 30 percent calcium chloride solution at 40 degrees C, previous to the sodium chloride treatment. The calcium chloride solution was renewed after the first, second, and third week.

According to his comments, Chatterji believed that the calcium chloride solution leached out the calcium hydroxide, and thus prevented the damage from alkali-silica reactions to occur.

Even if dissolution of calcium hydroxide by "mutual diffusion" is possible, it seems far more probable that the calcium hydroxide phase becomes transformed to a calcium chloro-hydroxide phase, which may occur without damage at the high temperature used.

At the subsequent treatment with sodium chloride solution, calcium ions in the pore solution gradually are substituted by sodium ions, and the calcium hydroxide will be the stable phase again. It would be interesting to know, after completed sodium chloride threatment, whether the specimens contain calcium hydroxide or not.

There is not stated in the literature that well measurable amounts of calcium hydroxide are extracted, or otherwise lost, when Portland cement mortar is stored in sodium chloride solution, even in saturated solution.

Probably, the calcium chloride treatment provokes the reaction (16) to happen, and no more tetracalcium aluminate ferrite can be available for the reaction (17), and no sodium hydroxide can be generated.

When Jespersen and Krogh (1976) reported that calcium hydroxide had disappeared when alkali silicate gel had formed, this probably was a consequence of reactions between copious amounts of alkali silicates and calcium hydroxide:

(19) $$Ca^{2+} + 2OH^{-} + 2HO\text{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}\text{-}O^{-} =$$

$$= HO\text{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}\text{-}O\text{-}Ca\text{-}O\text{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}\text{-}OH + 2OH^{-}$$

A solid phase of calcium silicate is formed, and two hydroxide ions are liberated, capable to attack more reactive silica minerals, if any. For the reaction to take place, the pH value should not be much higher than 12.5. Probably, at this pH level, two or possibly three times more calcium hydroxide will enter the calcium silicate after it was formed according to (20), but probably only one hydroxide ion will be liberated for each molecule of silica, SiO_2.

Thus, the observed loss of calcium hydroxide probably is a result of, and not a prerequisite for, the alkali-silica reaction.

When stored in saturated sodium chloride solution, slag cement mortar has, according to Smolczyk (1968), lost 2/3 of its content of solid calcium hydroxide, compared with the content after storing in pure water. Normally, a hardened and well cured paste of slag cement with 75 percent slag never contains much calcium hydroxide.

The statements indicate that solid calcium hydroxide remains stable, also when immersed in saturated sodium chloride solution, except the amount which is consumed for forming calcium chloro-aluminate hydrates according to (16).

REFERENCES

Bonzel, Justus, and Locher, Friedrich Wilhelm, "Ueber das Angriffsvermögen von Wässern, Böden und Gasen auf Beton. Anmerkungen zu den Normentwuerfen DIN 4030 E und DIN 1045 E". Beton (1968) pp 401-404, 443-445.

Calleja, J, "Durability." 7th International Congress on the Chemistry of Cement, Paris (1980). Principal Report VII-2/(1-48).

Chatterji, S, and Damgaard Jensen, A, "Studies of the mechanism of calcium chloride attack on Portland cement concrete." Nordisk betong 19 (1975) (5), 5, 6.

Chatterji, S, "The Role of $Ca(OH)_2$ in the breakdown of Portland cement concrete due to alkali-silica reaction." Cement and Concrete Research Vol 9, pp 185-188 (1979).

Jespersen, Mogens J, and Krogh, Hanne, "Undersøgelse av Holdbarheden af Mørtelprøver i NaCl-opløsninger." Nordisk Betongforskningsmøte, Oslo 23-25 august (1976), Nordisk Betongforbund.

Kalousek, G L, and Benton, E J, "Mechanism of seawater attack on cement pastes." J Am Concrete Inst, 67 (1970),187-192.

Midgley, Henry G, and Illston, J M, "Effect of Chloride Penetration on the Properties of Hardened Cement Pastes." 7th International Congress on the Chemistry of Cement, Paris (1980). Communication VII-(101-103).

Nielsen, John H, and Krogh, Hanne, "Undersøgelse af Holdbarheden af Mørtelprøver i $CaCl_2$-opløsninger." Nordisk Betongforskningsmøte, Oslo 23-25 august (1976), Nordisk Betongforbund.

Riedel, W, "Die Korrosionsbeständigkeit von Zementmörteln in Magnesiumsalzlösungen." Zement-Kalk-Gips, 26 (1973), 286-296.

Seidel, A, "Solubilities of inorganic and metal organic compounds." van Nostrand, New York (1940).

Smolczyk, Heinz G, "Chemical Reactions of Strong Chloride-Solutions with Concrete." Proceedings of The Fifth International Symposium on the Chemistry of Cement, Tokyo (1968). Supplementary Paper III-31, 274-280.

Suzukawa, Y, "Resistance of Hardened Cement Mortar to Magnesium Chloride Solution." 7th International Congress on the Chemistry of Cement, Paris (1980). Communication VII (124-126).

Ushiyama, H, and Goto, S, "Diffusion of various ions in hardened Portland cement paste." The VI International Congress on the Chemistry of Cement, Moscow, September (1974), Supplementary Paper, Section II, II-3, II-4, II-5.

Wannerberg, C, "Saltskador på betongbroar." Stadsbyggnad 1982 - 1, Stockholm.