

# Delayed Ettringite Formation in Concrete

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## 1. Introduction

The problem of durability of concrete with cement as binding material comes more and more to the fore with the increased use of concrete, with the changed production and utilization conditions, and with the further development and adaptation of concrete properties by changing concrete composition. Processes in connection with the ettringite formation in concrete are belong to the partly unsolved problems. While the primary ettringite formation in the initial stage of the hydration is seen as a positive effect because it enables the setting regulation, a damaging role is often attributed to the ettringite formation in hardened concrete. Damaged concretes often show large amounts of ettringite in structure damages even if they were not exposed to heat treatment (e.g. pavement concrete).

One of the first publications about concrete-damaging late ettringite formation appeared in 1945 by Lerch [1]. Kennerly of New Zealand [2] gave a report of similar findings in 1965, and Volkwein [3] in 1979. A characteristic feature of this type of damage is the conspicuous formation of ettringite in voids, cracks, and the contact zone between the aggregate and the hardened cement paste without any external sulfate attack having taken place. Damage in conjunction with ettringite formation in hardened concrete was first identified in heat-treated, precast concrete elements which, during use, had been exposed to open-air weathering with frequent wetting. The concretes affected were mainly high-grade concretes of high strength and low porosity. Conspicuous formation of ettringite in distorted micro-structural defects and in voids is also being observed increasingly in conjunction with damage in concrete components which have not been heat-treated. Investigations have now also been carried out into this formation of new phases, known as late ettringite formation, which takes place under normal ambient conditions in concretes which have not been heat-treated.

After carrying out extensive investigations different hypothesis were developed by many authors on how ettringite formation in hardened concrete and therefore a damage mechanism can be initiated, and it is said that the formation mechanism [4-6] and different ettringite modifications [7] play an important role. It was found that a heat treatment at higher temperatures [8-13], influence of frost- or freezing-thawing [14, 15], carbonation processes [16, 17], moisture affect [18] and with it moisture and temperature changes such as occurring under natural conditions [19, 20] can cause ettringite formation in hardened concrete. A complex occurrence of ettringite formation and further crack causing damage mechanisms such as ASR was found [21-24]. An ettringite formation in hardened concrete does not in every case lead to a direct damage of the concrete structure. At present, there is still controversy whether different types of ettringite exist; whether the damage mechanism can be initiated by coarse- or fine-crystalline ettringite; whether the formation of large ettringite crystals in hardened concrete, which also occur without heat treatment, is the primary cause of damages in the micro structure or if it only causes damage-promoting changes in the micro structure; and which practical consequences the ettringite filling of artificial air voids may have.

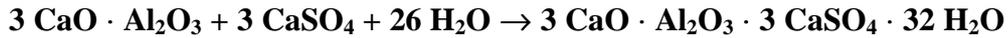
Despite extensive investigations in connection with ettringite formation, the direct cause of damage, the chronological development of the concrete damaging mechanism, and the role of

different influences such as pre-damages, sulfate, and alkali content were not yet clearly solved.

The presence of ettringite crystals in the concrete is frequently equated with harmful ettringite formation. So far, however, no clear connection has ever been proven between the emergence of cracks and the recrystallization of ettringite. Similarly, calcite in concrete cracks is not the cause of the cracks, the cracks emerge as a consequence of other damage mechanisms, e.g. mechanical stresses, shrinkage, or expansive reactions.

## 2. Ettringite in fresh concrete

According to the latest findings the primary ettringite formation from  $C_3A$  and gypsum in the presence of calcium hydroxide puts into action right after water addition:



This reaction ends as soon as the sulfate concentration, needed for forming the ettringite, decreases below the limit. From this point the remaining  $C_3A$  reacts by partly solution of the already formed ettringite to monosulfate and solid solutions between  $C_3A \cdot \bar{S}H_{12} - C_4AH_{13}$  which in aqueous solution again form ettringite and tetracalcium aluminate hydrate. The compound  $SO_3$  with a percent of 9.1, i.e. 19 % gypsum, would be necessary, for example, to transform 10%  $C_3A$  fully into ettringite. However, in accordance with EN 197-1, the sulfate content is limited to a maximum of 3.5 to 4 %, depending on the type and strength class of the cement. Therefore, monosulfate is always formed as well.

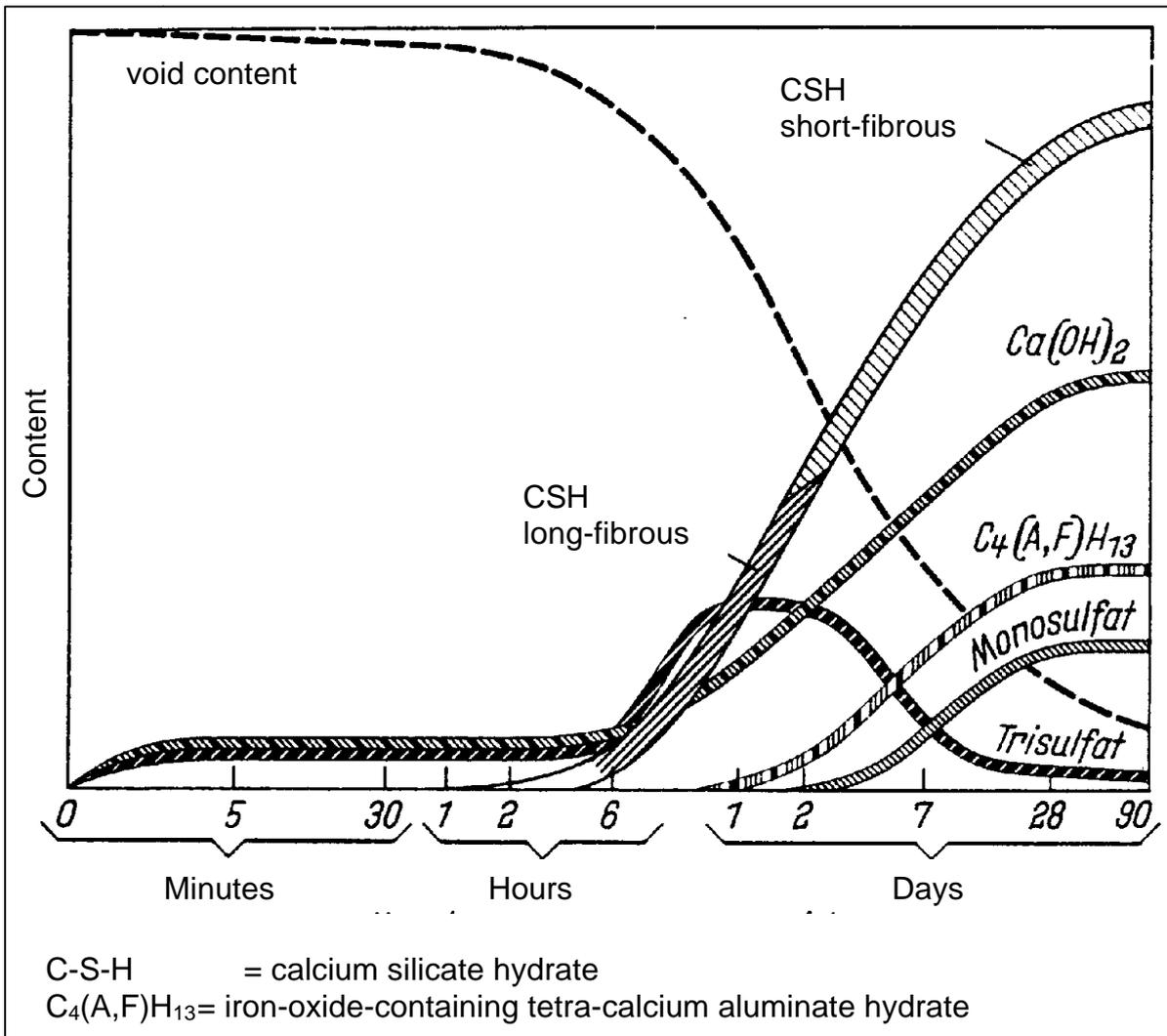


Abb. 1: Schematic representation of the formation of hydrate phases and the structure development during cement hydration according to [74]

Therefore, the sulfate deficit which occurs during hydration due to the consumption of sulfate is the cause of the decomposition of the ettringite. The ettringite decomposition at high alkali contents must begin earlier, because with increasing alkali content for the ettringite formation higher sulfate contents in the solution phase are necessary [32]. If the decomposition of the primary ettringite is not completed, then ettringite as well as monosulfate occurs in the normal hardened concrete (fig. 1). During the first hours of hydration shape and size of the ettringite and monosulfate crystals mainly change in dependence of the solution composition and due to this the setting behavior is influenced [75].

Ettringite ( $C_6A \bar{S}_3H_{32}$ ) forms hexagonal-prismatic crystals. According to the structure model by TAYLOR [76], the crystals are based on columns of cations of the composition  $\{Ca_3[Al(OH)_6] \cdot 12 H_2O\}^{3+}$ . In there, the  $Al(OH)_6^{3-}$ -octahedra are bound up with the edge-sharing  $CaO_8$ -polyhedra, that means each aluminum-ion, bound into the crystal, is connected to  $Ca^{2+}$ -ions, with which they share  $OH^-$  ions. The intervening channels contain the  $SO_4^{2-}$ -tetrahedra and the remaining  $H_2O$  molecules (fig. 2). The  $H_2O$  molecules are partly bound very loose into the ettringite structure. Due to this, the easy slit off of part of the water during drying or increased temperatures can be explained and, therefore, the existence of ettringite with different crystal water contents.

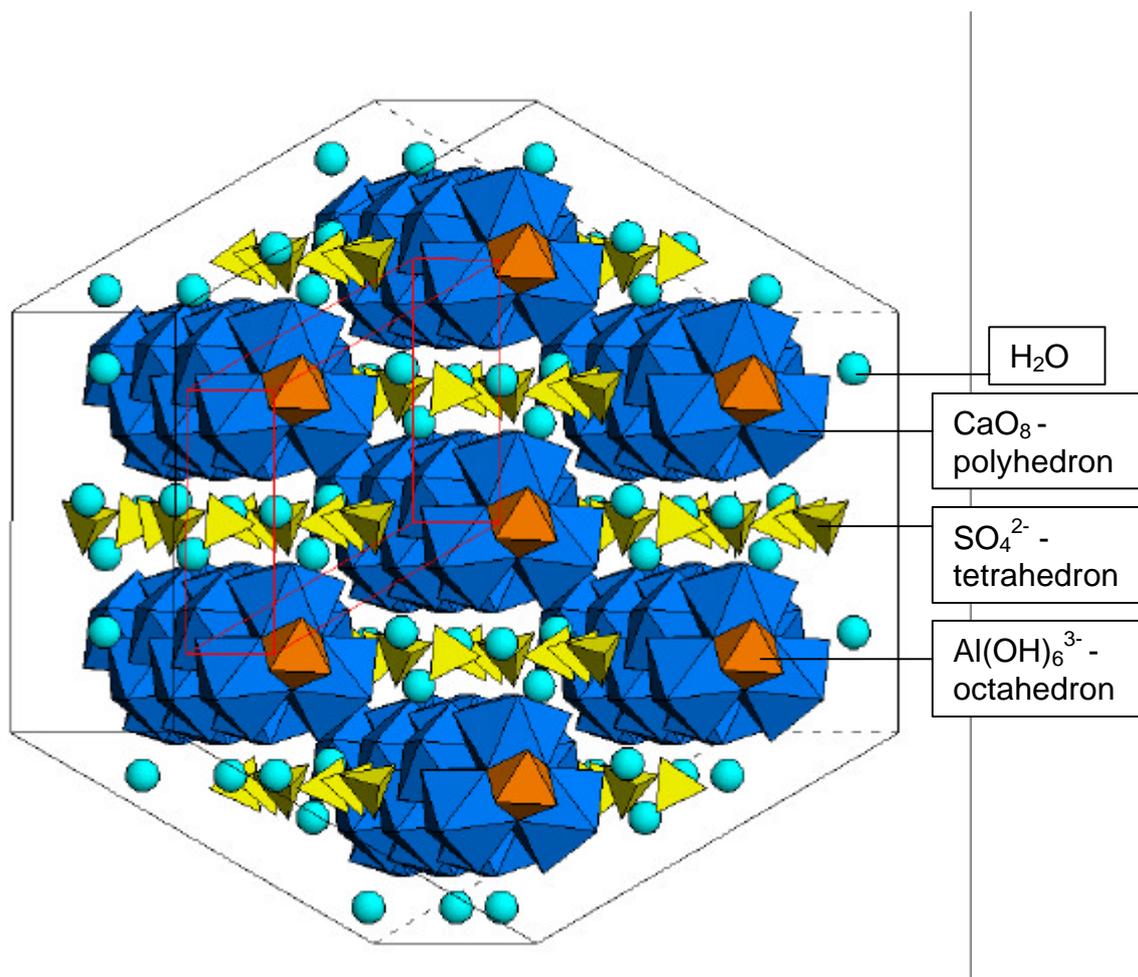


Abb. 2: Structure model of ettringite  
(according to Dr. J. Neubauer/University Erlangen/Germany)

### 3. Ettringite in hardened concrete

Scanning electron photomicrographs show that ettringite ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ) occurs in concrete in various forms, often as spherical clusters of ettringite crystals, felt-like or parallel needles of differing sizes. If ettringite crystallizes out without spatial obstruction, e.g. in pores, then it has the typical needle-shaped crystal habit.

Investigations at the Bauhaus-University Weimar into the crystal habit of ettringite by means of an environmental scanning electron microscope (ESEM), i.e. with no influence by the method of preparation (drying, vapor deposition, high vacuum), were carried out on ettringite present in severely damaged concretes and on synthesized ettringite. It was found that the fairly large, needle-shaped ettringite crystals (thickness in the  $\mu\text{m}$  range) found previously during the scanning electron microscope (SEM) investigations under high vacuum often consisted of many parallel, very slender, crystals with thickness in the range between 20 and 200 nm lying close to one another (Figs. 3, 4), regardless of whether the ettringite crystallized with or without spatial obstruction in the concrete or formed synthetically in a solution. By investigations with SEM a vapor deposited carbon layer with a thickness of about 30 nm was necessary but covered up the fine structures.

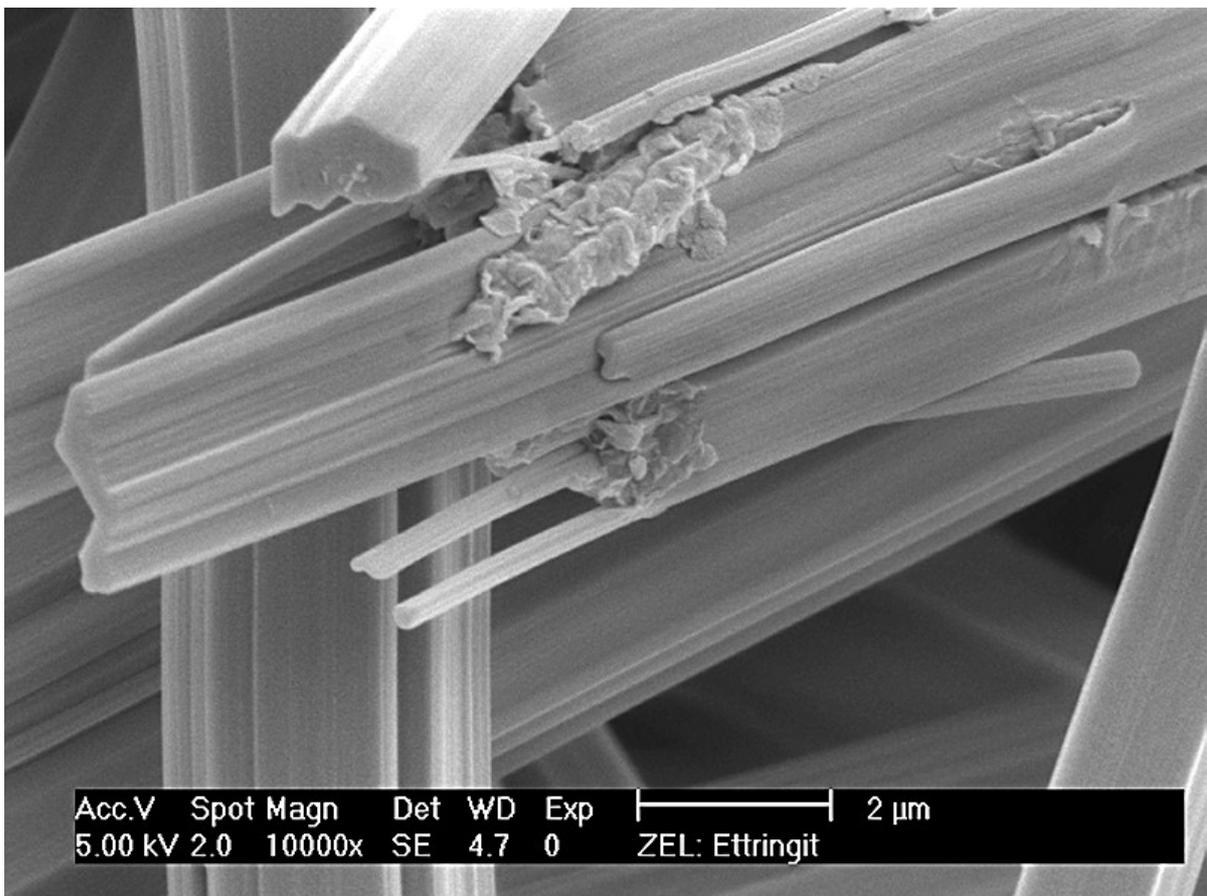


Fig. 3: Very slender ettringite crystals with thicknesses in the range between 20 and 200 nm lay close to one another and form thick needle-like appearing formations; no carbon coating; in ESEM in an atmosphere of water vapor

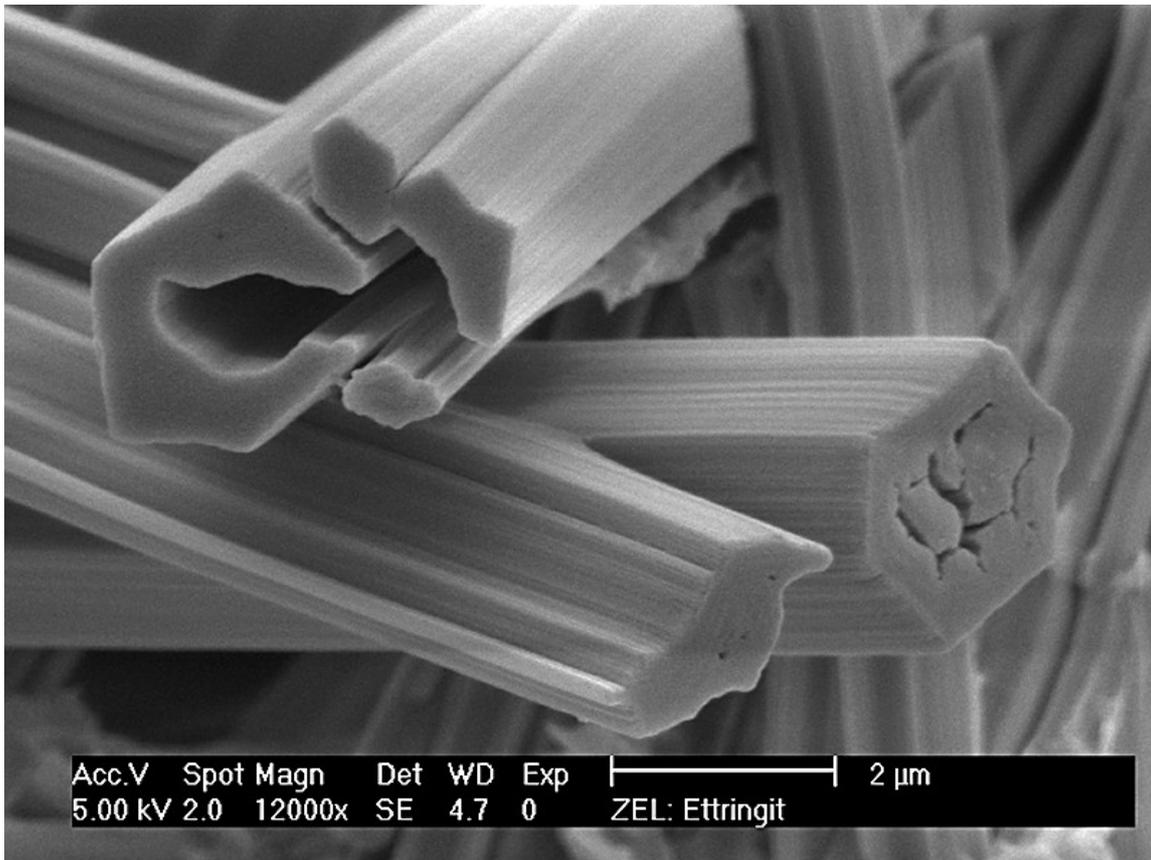


Fig. 4: Very slender ettringite crystals forming needle-shaped formations with hexagonal cross-section and a thickness of about 2  $\mu\text{m}$ ; no carbon coating; in ESEM in an atmosphere of water vapor

The causes of the many different forms in which ettringite appears are not yet fully explained. Some influencing factors seem to be the composition, the concentration conditions and the pH value of the concrete pore solution [7, 9, 25-28], as well as the formation mechanism (through-solution mechanism or solid state reaction), the inclusion of foreign ions, etc. According to Chartschenko's investigations in [27, 28], for example, the length-thickness ratio of synthesized ettringite crystals is extremely dependent on the pH value of the reaction solution (Fig. 5). Long, fiber-shaped crystals were formed at pH values between 10 and 12, but extremely microcrystalline ettringite was present at pH values above 13.0.

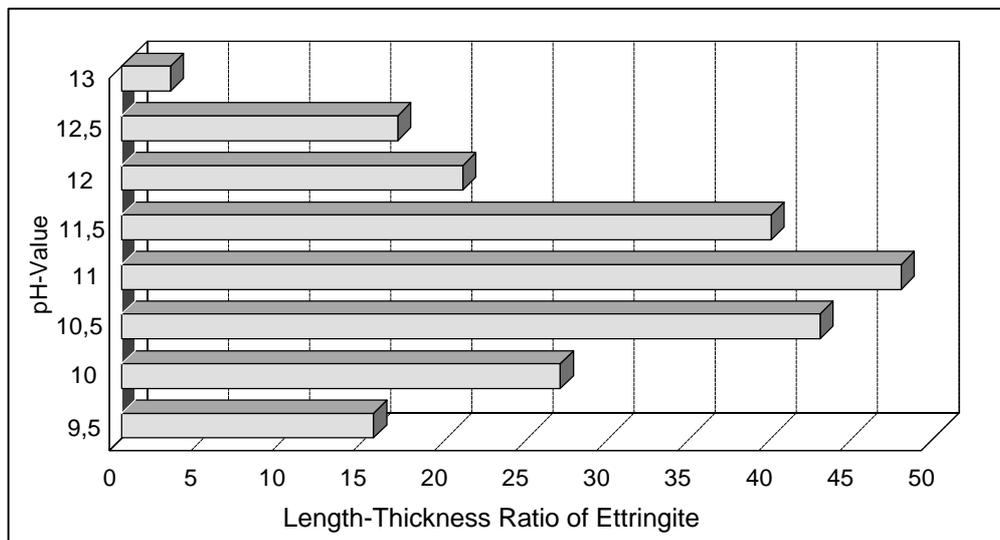


Fig. 5: Change in ettringite habit (length-thickness ratio of the ettringite crystals)

as a function of pH in the reaction solution according to [27, 28]

Mehta [7] describes two modifications of ettringite which differ in habit and size. The long, lath-like crystals which could be 10 to 100  $\mu\text{m}$  long and several  $\mu\text{m}$  thick and formed at low hydroxyl ion concentrations, i.e. with low pH values in the pore solution, were designated by Mehta as Type I. If hydrated cements contain considerable amounts of these large ettringite crystals, this leads to high strengths, but not to expansion effects. Mehta therefore proposed that Type I ettringite as not expansive. The rod-like crystals which are only 1 to 2  $\mu\text{m}$  long and 0,1 to 0,2  $\mu\text{m}$  thick or even smaller, and which form at high hydroxyl ion concentrations which are present during the hydration of portland cements were taken by Mehta as Type II ettringite. According to Mehta, fairly large quantities of this microcrystalline ettringite can cause expansion effects through water adsorption.

Damage mechanisms on concrete are often brought in connection with the appearance form and formation mechanism of ettringite.

#### 4. Problematic

It has been assumed so far that in normally hardened concrete the formation of ettringite which begins immediately during hydration is completed after about 24 h. The ettringite is said to be then distributed evenly in the hardened cement paste, probably in a microcrystalline form. Using SEM and microanalysis it cannot be located with certainty either in the microstructure or in the existing spaces such as capillaries or air voids, etc. In most cases, it is also not possible to detect ettringite in the concrete by X-ray diffraction or differential thermo-analysis.

After comparison of published data on the stability domain of ettringite [e.g. 1, 25-33] and the composition of the pore solution in the hardened cement paste [e.g. 9, 34-41], mortar, or concrete, meaning the existence medium of the hydrate phases, the question arises whether or not ettringite can still exist in the hardened cement paste.

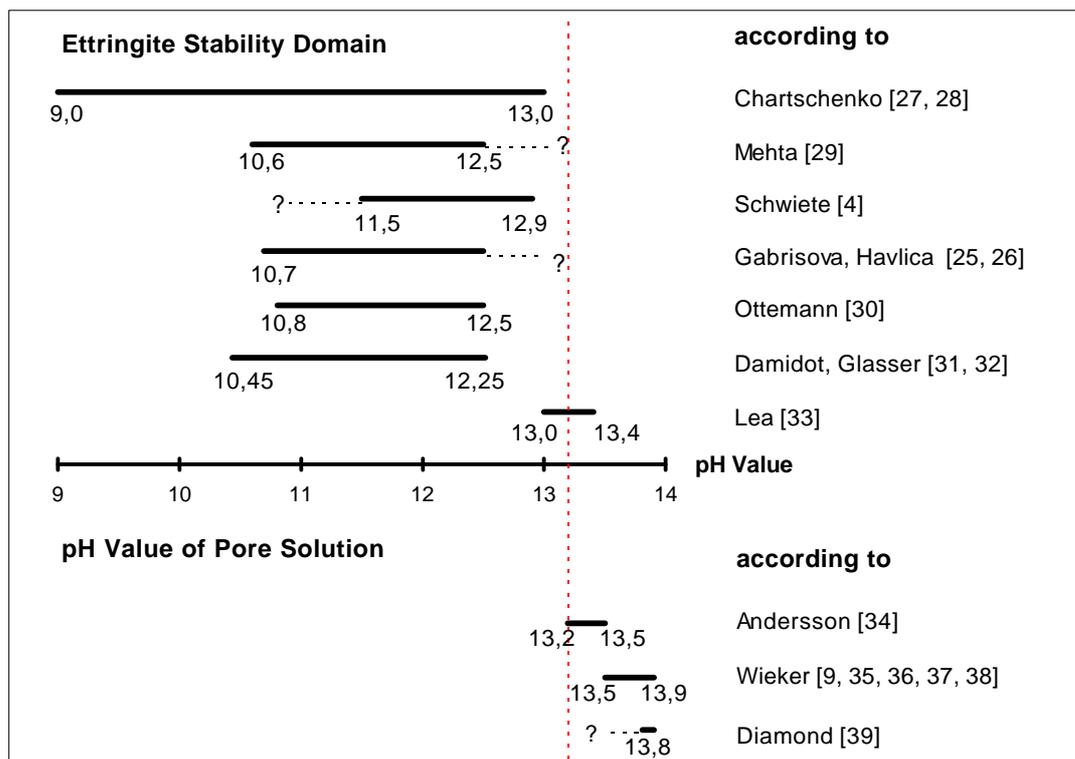


Fig. 6: Comparison of stability range of ettringite and pH range of pore solution according to literature

Note: The calculation of the pH value from the OH-ion concentration ( $H^+$ -ion concentration) is normally only possible, if the total concentration of the solution is set not above 0.1n. For the assessment and comparability of the different specifications mentioned in literature in this presentation, however, a theoretical pH-value was calculated from the ion concentration, whereby the ion concentration was equated with the ion activity.

In concretes stored or permanently used in a dry climate (e.g. interior elements), ettringite is hardly detectable, even after many years of use. However, if a concrete is exposed to alternating moisture conditions during use, then ettringite crystals can be detected in the voids already after a short time (6 months) without evidence of any serious impairment of the properties of the solid concrete. A white layer enriched with ettringite is often found on aggregate surfaces. If the concrete has been heat-treated or if elevated temperatures occur during drying the effect of accumulation of ettringite in pores and contact zones between aggregate and hardened cement paste is enhanced. In damaged concrete, ettringite is also to be found in the cracks.

Therefore, it is necessary to clarify which processes in hardened concrete can lead to the observed accumulation of ettringite, and which mechanism makes „invisible“ ettringite visible. The correlations between the composition of the liquid phase in the hardened cement past, mortar, or concrete and the existence and stability of ettringite seem to be the decisive influence.

## 5. Present hypotheses on the formation of ettringite in hardened concrete

The possible causes of accumulation of ettringite in the hardened concrete are as follows:

- 1) additional formation of ettringite by internal sulfate release, e.g. from existing monosulfate or other sulfate-free phases, combined with transport processes, and
- 2) mobilization of existing ettringite and/or its constituents, their transport and recrystallization (with grain growth).

So far the investigations into ettringite formation in hardened concrete led to the following hypotheses:

### 5.1 Internal sulfate sources and late sulfate release

#### After heat-treatment

Ettringite formation in hardened concrete after heat-treatment is often traced back to temperatures in concrete above the stability limit of ettringite. With rising temperature there is a drop in the thermodynamic stability of ettringite in favor of monosulfate. Depending on the thermodynamic data the theoretical transformation temperature from ettringite into monosulfate ranges between 70 and 90°C. The stability limit of the ettringite falls with increasing alkali content in the pore solution as described by Wieker et al. [9, 36]. Concrete temperatures above the respective stability limit of the ettringite can lead to decomposition of the ettringite, e.g. with the formation of monosulfate and sulfate. With a subsequent drop in temperature the monosulfate becomes metastable so that, if there is sufficient water available (moisture effects) ettringite can be formed again.

According to Ludwig et al. [8, 42-46], these processes take place under the conditions of heat-treatment with subsequent moist conditions. But fairly high concrete temperatures can also occur during concrete placement under elevated external temperatures (summer weather) [47], can be attributed to the use of hot cement and/or can be a result of the liberated heat of hydration which cause temperatures of more than 70 °C, especially in massive concrete elements. Similar processes may occur in concretes which have not been heat-treated but during use are exposed to temperatures above the stability limit of ettringite and to varying

ambient moisture. The temperature of 60°C in concrete panels was found to be realistic under intensive sun-radiation by measuring the temperature in the upper layer of open-air stored concrete panels (fig. 7). Other authors also reported temperatures of 60°C to 80°C for dark surfaces which can occur e.g. in exposed concrete pavement segments, external wall elements, bridge segments, parking decks and so on [48-50].

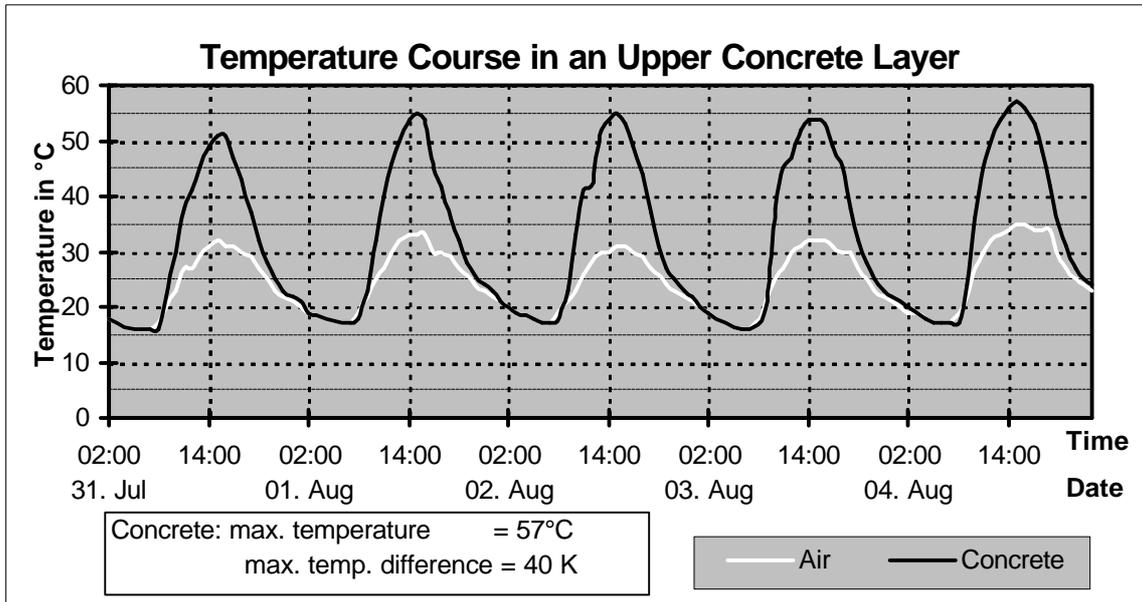


Fig. 7: Temperature course in the upper layer (5 mm) of a concrete slab which is exposed to natural weathering in Germany

According to recent investigations, the ettringite formation in hardened concrete after heat treatment can be traced back to the increased sulfate binding ability of C-S-H phases at elevated temperatures [12, 13, 51, 52]. According to current understanding, the majority of the  $\text{SO}_4^{2-}$  is adsorptively, i.e. physically, attached to the C-S-H and is therefore available as mobile sulfate which is available at later moisture storage of the concrete at lower temperatures. After heat-treatment ettringite is formed under service conditions (low temperature, elevated moisture) from monosulfate and  $\text{C}_3\text{AH}_6$  both with the  $\text{SO}_4^{2-}$  from the alkali sulfates in the pore solution and with the  $\text{SO}_4^{2-}$  attached to the C-S-H. This delayed ettringite formation takes place unless sulfate is supplied from outside.

Practical experience has shown that damage to concrete as a result of delayed ettringite formation due to heat-treatment can be avoided by complying with the “Guidelines for heat-treatment of concrete“, issued by the German Committee for Reinforced Concrete. This lays down specifications for the heat-treatment, such as the minimum duration for the pre-storage period and the maximum temperature of the concrete, depending on the expected exposure of the concrete to moisture under the conditions of use.

#### Freeze-thaw attack with and without de-icing salt

According to investigations by Stark and Ludwig, H.-M. [14, 15, 53-55], ettringite can be formed from monosulfate during freeze-thaw attacks with and without de-icing salt. Monosulfate is always formed during the hydration, as described above. Ettringite is very stable under freeze-thaw attacks, while monosulfate is partially transformed into ettringite [53]. The sulfate which this requires was not available before the frost attack occurred. It can therefore be assumed that the additional sulfate required is supplied by partial decomposition of the monosulfate due to carbonation or due to partial transformation of monosulfate into monochloride during the freeze-thaw attack with de-icing salt (fig. 8). Gypsum is liberated

during this process and can form additional ettringite with the not yet decomposed or transformed monosulfate.

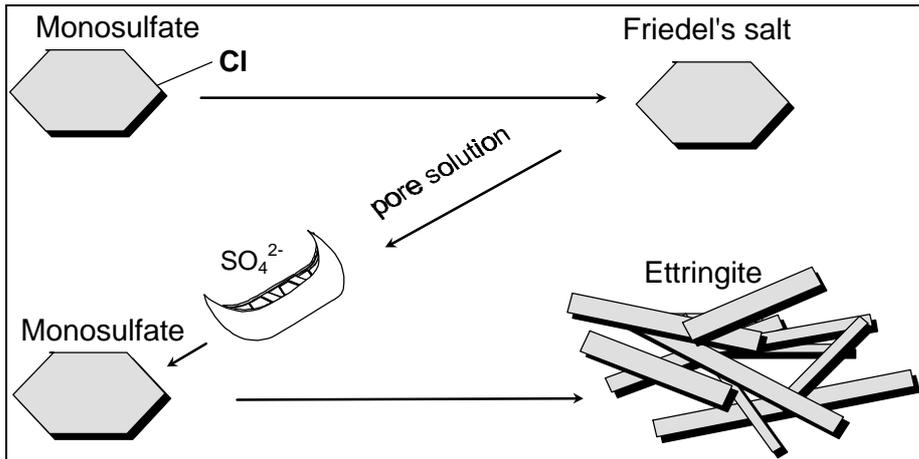


Fig. 8: Mechanism of ettringite formation under frost and de-icing salt attack

### Carbonation

A different model described by Kuzel et al. [16, 17, 56-58] explains the late or delayed ettringite formation from monosulfate under the combined action of  $\text{CO}_2$  and water. According to this, the monosulfate is decomposed by carbonation to form  $\text{CaCO}_3$ ,  $\text{Al}(\text{OH})_3$ , gypsum, and water via the intermediate stages of hemicarbonates and monocarbonates. The liberated gypsum is available for reaction with unreacted monosulfate to form ettringite. However, as the action of  $\text{CO}_2$  progresses, the ettringite structure is also destroyed with elimination of gypsum. It was not yet determined whether the ettringite formation through the carbonation is of practical importance.

### Clinker

It is suspected that the sulfate initially fixed in the clinker forms another internal source of sulfate [59]. This sulfate could be liberated by advancing hydration of the clinker components during use and therefore could be available for additional ettringite formation in the hardened concrete without any external supply of sulfate. However, cement clinker of normal composition cannot contain any anhydrite [60, 61] because at a kiln temperature of  $1450^\circ\text{C}$ ,  $\text{CaSO}_4$  is thermally decomposed into  $\text{CaO}$ ,  $\text{SO}_2$ , and oxygen. Only in  $\text{C}_4\text{A}_3\text{S}$  clinkers, which are produced at about  $1300^\circ\text{C}$  and are used for the production of expansive cements, anhydrite could occur in small quantities.

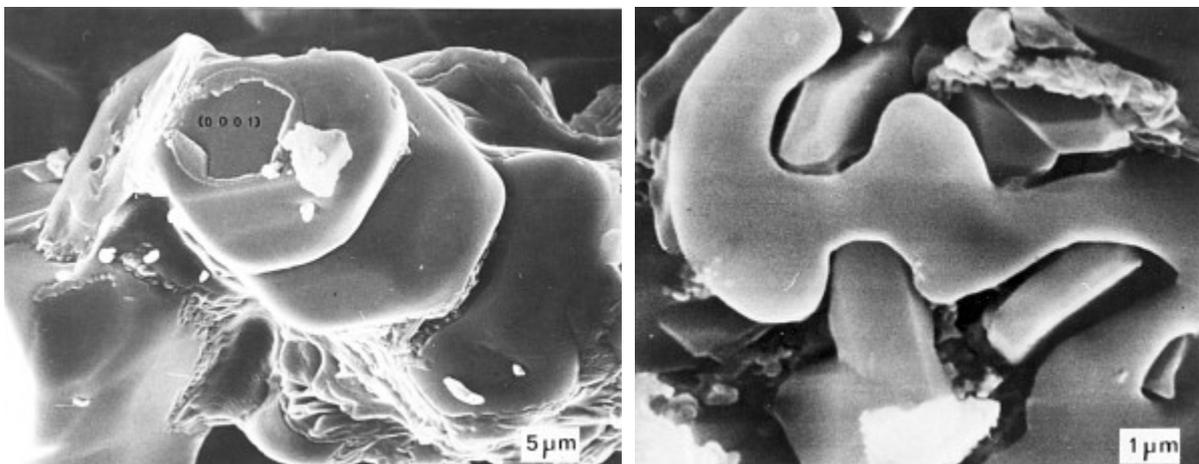


Fig. 9: a) Alkali sulfate formation

b) Alkali sulfate formation

on alite crystals  
in a portland cement clinker

in the structure  
of a portland cement clinker

Cement clinker in Central Europe nearly always contains more alkalis than sulfate; therefore, after the clinker is burnt, the sulfate is mostly combined as alkali sulfates.  $K_2SO_4$  is an independent phase in the clinker which does not mix with the clinker melt. It solidifies last and covers the alite and other clinker minerals with a thin layer (fig 9a, b). These alkali sulfates dissolve immediately in contact with water.

Only a very small quantity of sulfate, less than 0.5 %, is fixed in the clinker phases and is liberated only during the hydration progress. In practice, for normal clinker sulfate contents, this sulfate can be ruled out as an internal source of sulfate as an initiation of the formation of ettringite which could damage concrete. Common sulfate contents of characteristic cement clinker compositions are given in table 1.

Content in %	ordinary portland cement	high-early strength portland cement	sulfate resistant portland cements	white portland cement
SiO <sub>2</sub>	20.5	19.6	20.5	20.9
Al <sub>2</sub> O <sub>3</sub>	6.5	6.0	4.8	4.3
Fe <sub>2</sub> O <sub>3</sub>	3.5	3.3	6.2	0.5
CaO	64.4	66.6	61.8	66.7
CaO <sub>free</sub>	1.4	1.8	0.7	1.2
CaO <sub>effective</sub>	62.5	64.3	60.6	65.4
SO <sub>3</sub>	1.0	0.7	0.9	0.2
MgO	3.3	2.1	1.9	1.6

Tab. 1: Chemical composition of characteristic cement clinker

## 5.2 Alternating moisture conditions

Moisture can cause mobilization of the phase constituents in the concrete. Alternating moisture conditions lead to moisture gradients in the concrete. These produce moisture movements, transport of substances, concentration differences in the concrete microstructure, and transfer of substances with the surroundings, which can cause a change in the composition of the pore solution and a reduction in the content of water-soluble alkalis in the concrete.

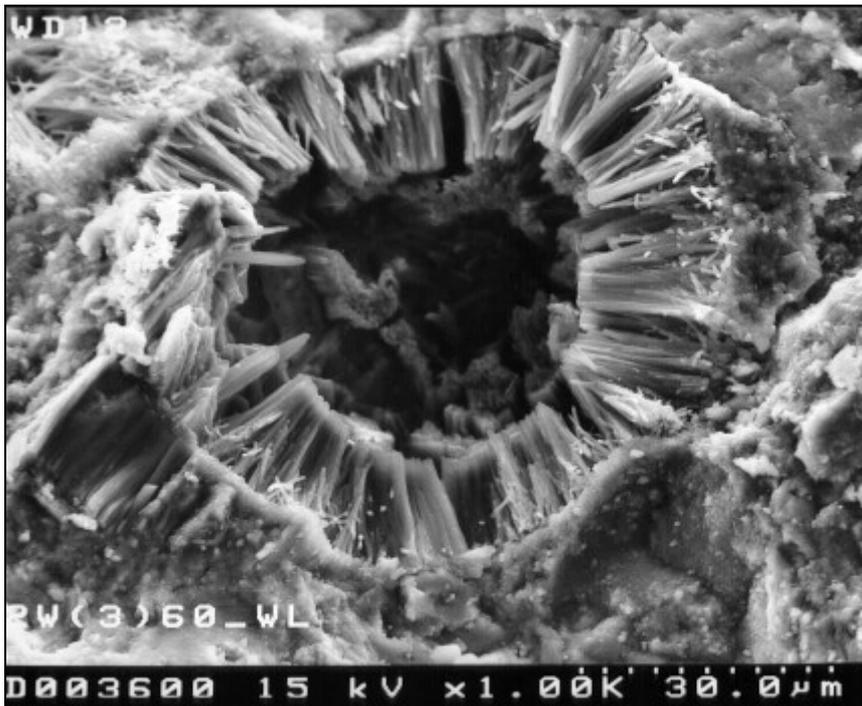


Fig. 10: Ettringite has - by directed crystal growth - partly filled an air void

Various investigation results (Johansen and Thaulow [6, 18, 62, 63], Scrivener and Wieker et al. [51, 64], Stark and Bollmann [19, 20, 40, 41, 65]) show that under these conditions an accumulation of ettringite in pores, cracks, and weak parts of the structure is promoted. It is assumed that ettringite formed at high pH values is most likely microcrystalline, amorphous to X-rays, and less stable; therefore, it gradually dissolves in the pore liquid of a moist concrete and recrystallize. Transport processes taking place in the capillaries are interrupted by air voids, cracks, and contact zones between aggregate and hardened cement paste, for example. In such places this leads to enrichment of the transported substances and could also explain the observed accumulation of ettringite in the air voids (fig. 10) which were previously filled with air or water.

### 5.3 Marginal conditions which promote damage

#### Predamage to the concrete

Every concrete contains weak points and micro damage to the internal structure, e.g. pores, distorted transition zones between aggregate and hardened cement paste, cracks. They do not necessarily impair the quality of the hardened concrete (strength, modulus of elasticity etc.), but they can promote the transport of moisture and phase forming components and therefore aid ettringite crystallization. Physical causes for this, can, for example, be a segregation phenomena caused by compaction (faults in the contact zone between aggregate and hardened cement paste and in the areas close to the surface); stresses in the microstructure through temperature or moisture gradients; differing thermal expansion coefficients of the concrete constituents, shrinkage, mechanical stresses, and freeze-thaw attack with and without de-icing salt. Microstructural damages can be produced chemically by expansion reactions (alkali-silica reaction, free CaO or MgO) and chemical shrinkage (self-desiccation at  $w/c' \leq 0.3$ ).

#### Influence of the pore volume

If the transport of moisture and phase components can take place in the concrete microstructure, then very dense concretes, with low porosity and fine-pored microstructures, are more sensitive under otherwise identical conditions than less dense concretes of higher porosity and coarse-pored microstructure. The reason for this is that concretes with fairly high

water-cement ratios or entrained air voids have a greater potential expansion space for the formation of new phases.

Because of the great importance of the pore structure for concrete-damaging late ettringite formation, the results of investigations on mortar prisms cannot be applied directly to concrete.

#### Cement content and concrete composition

High cement contents not only result in higher concrete temperatures during hydration, but also increase the quantity of potential reaction partners for ettringite formation and, as a result, the quantity of ettringite per volume unit of concrete. This also increases the probability that the pore volume will not be sufficient to take the quantity of ettringite produced in the already hardened concrete.

A CEM I 42.5 R cement with a  $C_3A$  content of 7.6 % (calculation according to Bogue) and an  $SO_3$  content of 2.3 % can, at most, form 12.02 g ettringite/100 g cement. With a cement content of 300 kg/m<sup>3</sup> concrete and an ettringite density of 1.77 g/cm<sup>3</sup>, it corresponds to a volume of 2.04 % ettringite in a cubic meter of concrete. If, with the same cement content, the sulfate content of the cement is increased to 4.0 %, then this results in a maximum ettringite volume of 3.54 % by volume. With increasing quantity of cement, there is a corresponding increase in the proportion of ettringite by volume. This is contrasted with an average pore volume in solid concrete of 9 to 15 % by volume in normal concrete, therefore, in concrete with a normal composition the maximum amount of ettringite that can be formed is smaller than the total pore volume. This indicates that it is not the total pore volume but rather the pore size distribution which must be of decisive importance for the degree of damage.

Portland cements (apart from highly sulfate-resisting cements) always have excess  $C_3A$  relative to sulfate, so the sulfate governs the maximum quantity of ettringite that can be formed. This is the reason why the sulfate content is often held responsible for the occurrence of concrete damage. However, so far no clear connection has been proven between the normal sulfate levels in Portland cement and the expansion of the concrete, the occurrence of damage, and the degree of damage.

As already mentioned, the alkali content of the cement affects not only the temperature-dependent stability limit of the ettringite, but also the composition and the pH of the pore solution in the concrete, which, according to Mehta [7], affects the ettringite, whether forming fine or coarse crystals. The alkali levels in the range between 0.8 and 1.2 %  $Na_2O$ -equivalents, which are normal in portland cements, always lead to pH values between 13.5 and 14 during the initial hydration with low water-cement ratios (Fig. 6). The question arises whether the ettringite can be formed under these conditions or whether formed ettringite remains stable. If there is no carbonation or leaching while the concrete is in use, then these high pH values remain and the ettringite therefore retains its initial form.

## **6. Further hypotheses on the formation of ettringite in hardened concrete**

The temperature dependent stability of ettringite is often cited for explanations, but cannot be the cause for ettringite enrichments in many damage cases on non-heat treated concretes and on concretes damaged by ASR. As already mentioned, a decisive influence seem to have the connections between composition of the pore solution in hardened cement paste, mortar, or concrete and the existence- and stability range of ettringite.

### **6.1 Pore Solution**

### 6.1.1 Composition of the Pore Solution

According to the latest findings, the composition of the pore solution can be best determined after a phase selection solid-liquid by means of squeezing the pore solution out of the hardened cement paste under high pressures of 320 MPa [66] up to 375 MPa [34] and analysis of ion concentrations in the liquid phase.

In the early phase of hydration, as long as still unhydrated parts are available, the ions in the solution phase are not in thermodynamical balance with the solid materials because this condition is determined by permanent solution and precipitation processes. Therefore, hydration times of 28 days and more were mostly set for the assessment. The chronological development of the ion concentration shows that for most cements no substantial changes in the pore solution composition are to be expected after these periods.

The main part of the alkalis goes into solution with the beginning hydration. The further increase of the concentration is attributed to the consumption of the solution phase during hydration. At water-cement ratios of 0.5, the pH value of the pore solution in the hardened cement paste of most of the common portland cements (except low-alkali cements) is higher than 13.6 already after 1 day. Due to the further consumption of the solution phase during the ongoing hydration, the pH value increases and reaches values higher than 13.8 already after 28 days (fig. 11). In practice essentially lower water-cement ratios are often used so that the ion concentrations are much higher due to the low content of solution phase. This means that the medium surrounding the hydrate phases shows mostly OH-ion concentrations above 600mmol/l.

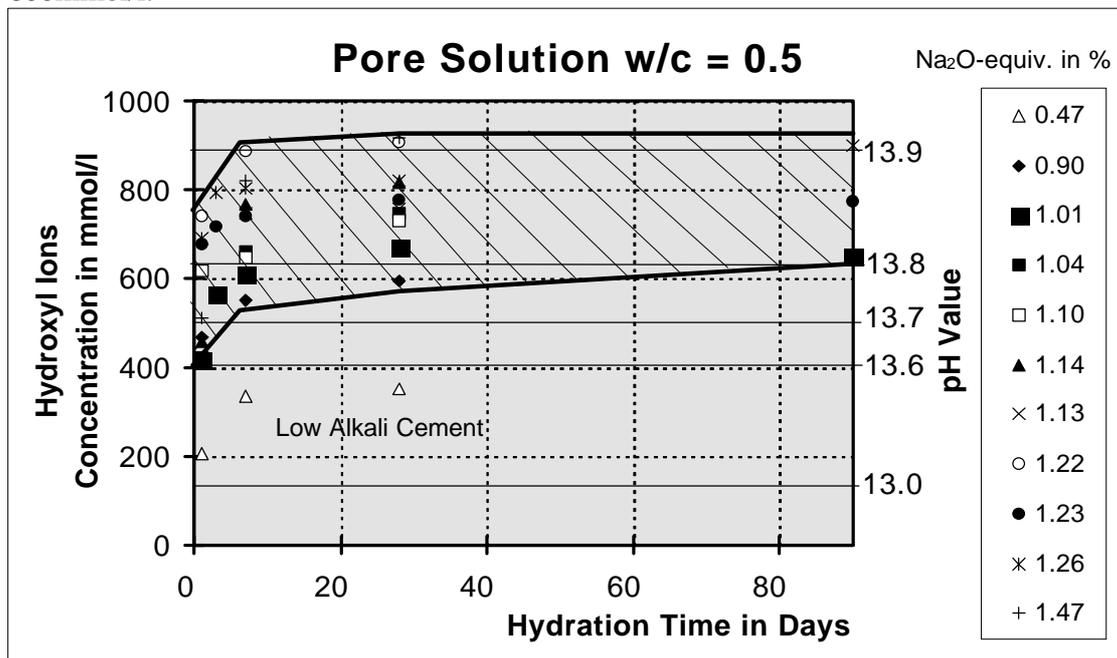


Fig. 11: OH-ion concentration and pH value of pore solution of different cements CEM I (ordinary portland cements; compressive strength of 32,5 N/mm<sup>2</sup> after 28 days- filled symbols; compressive strength of 42,5 N/mm<sup>2</sup> after 28 days- blank symbols)

### 6.1.2 Influences affecting the composition of the pore solution

In concrete elements which were affected by natural climate changes during service life, the composition of the pore solution inevitably changes due to the influence of moisture. While

this process goes on slowly in less-permeable structures and mainly affects the areas close to the surface, the high capillary porosity and micro damages can promote this process so that deeper areas could be affected faster. The alkali content and with it the OH-ion content in the pore solution can strongly be reduced by the above described process.

This becomes evident through tests on very small hardened cement paste- and mortar prisms (10mm x 10mm x 100mm) which were exposed to continuous storage under water or in air already after 1 day. After a storage time of 1 year, the chemical analysis clearly shows that the content of water soluble alkalis is strongly reduced (fig. 12), which therefore affects the composition of the pore solution regarding the pH value reduction. Furthermore, after continuous storage in water, the content of strongly bound alkalis is lower than after storage in air so that one can safely assume that the originally strongly bound alkalis in the cement are also available in water soluble condition during hydration. Thereby the Na<sub>2</sub>O-content, which only is about 1/5 of the K<sub>2</sub>O-content, is reduced in the same way like the K<sub>2</sub>O-content. Due to the continuous storage of the samples in water and the resulting leaching process occurring at the same time, the content of alkalis which are strongly bound in the hydration products is lower. On the other hand, the content of sulfates remains the same, independent of the type of storage (fig. 12), so that this reactant which is necessary for the ettringite formation will also be available with continuous storage in water.

Besides external influences which can lead to a reduction of the pH value, other mechanisms can influence the composition of the liquid phase. The integration of alkalis into the reaction products belongs to this. The boundage of alkalis into the alkali-silica gel e.g. also leads to a reduction of the alkali content in the surrounding solution.

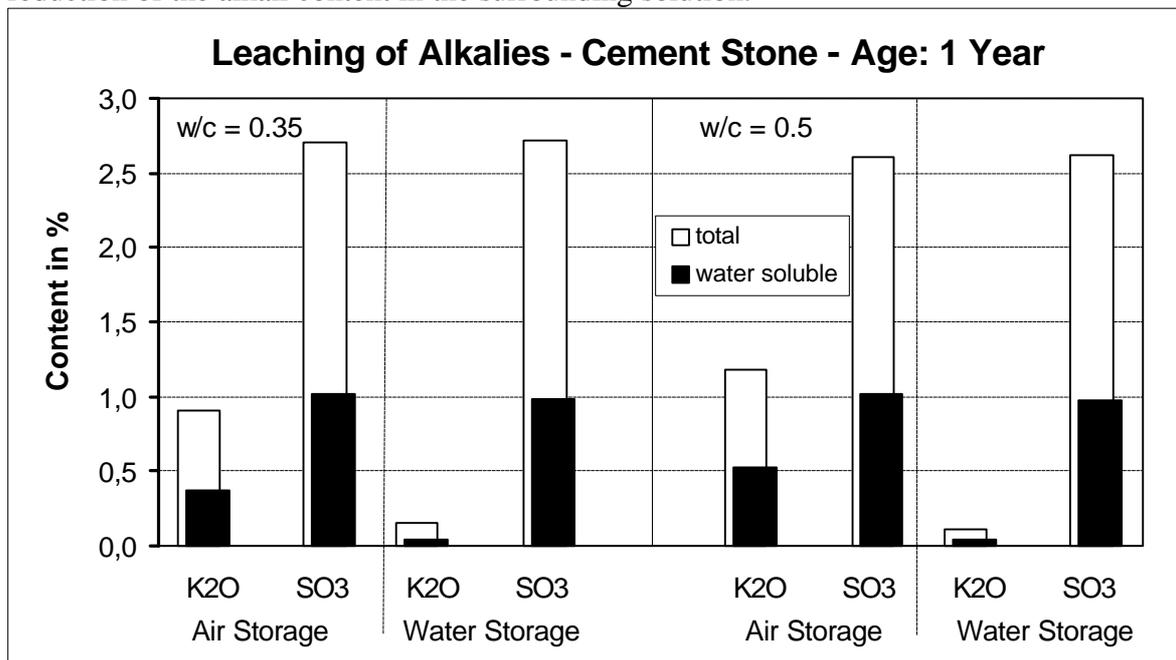


Fig. 12: Alkali and sulfate content of cement stone samples after 1 year storage in water and air

## 6.2 Ettringite

### 6.2.1 Synthesis

Ettringite occurs only in minimal amounts in concrete and hardened cement paste, so that analytical investigations are more difficult or are nearly impossible. For this reason model systems were used for the investigations. By stoichiometrical composition of the reaction

components ettringite precipitated from the solution, whereby in essence no other solid reaction products were synthesized. The pH value of the medium depends on the ions remaining in the solution under equilibrium conditions in dependence of solubility and stability of the ettringite. The measured pH value was set at 10.7. According to investigations in [25, 26], the value of 10.7 was set as the minimum limit for the stability of ettringite.

In systems with cement as binding material, the pH value normally depends on the alkalis and is set, as described, in an area above the pH value of 13.0. Therefore, the pH value was varied in model tests by the addition of KOH to the reaction solution. Measuring the pH value in such highly concentrated alkali hydroxide solutions is very problematic and faulty; therefore, the theoretical pH value calculated from the OH<sup>-</sup>-ion concentration was used again.

From an OH<sup>-</sup>-ion concentration of 320 mmol/l (theoretical calculated pH value 13.51), not only ettringite but also monocarbonate was increasingly formed. Ettringite was formed in small amounts up to an OH<sup>-</sup>-ion concentration of 370 mmol/l, meaning a theoretical pH value of 13.57. From an OH<sup>-</sup>-ion concentration of 400 mmol/l (theoretical calculated pH value 13.6), only the sulfate-free compounds monocarbonate and portlandite (calcite) were essentially established as crystalline reaction products by means of XRD (fig. 13), whereby the sulfate content of the solution phase increased. The formation of monocarbonate as well as calcite was attributed to the fact that the investigations could not be carried out in a CO<sub>2</sub>-free atmosphere, so that an eventual formation of monosulfate could not be proven.

Under the chosen test conditions (influence of OH<sup>-</sup>-ions and CO<sub>3</sub><sup>2-</sup>-ions), no ettringite formation was possible at pH values above 13.6 as it occurs at normal portland cements already after one day of hydration and at water-cement ratios of 0.5. Low-sulfate or sulfate-free reaction products were formed which are unstable and therefore carbonate easily under CO<sub>2</sub>-influence. The dependence of the ettringite morphology on the OH<sup>-</sup>-ion concentration in the reaction solution, often mentioned in literature, was not proven in the investigations carried out by means of the Environmental Scanning Electron Microscope.

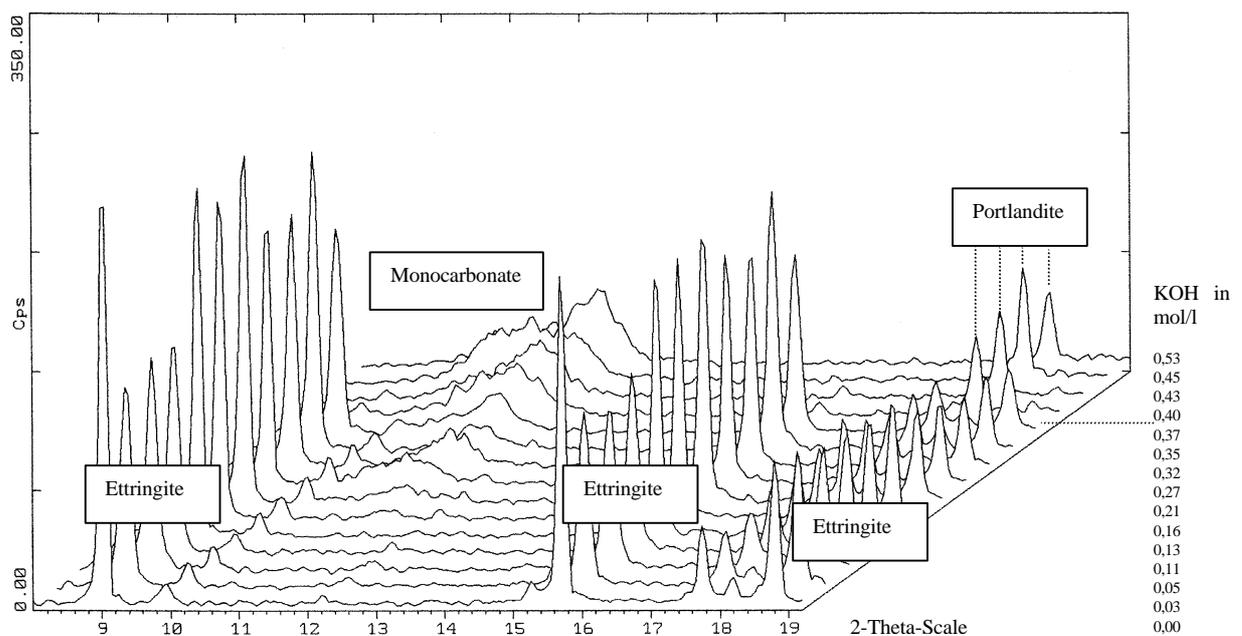


Fig. 13: X-ray analysis of ettringite synthesis tests, different KOH-concentrations in the reaction solutions

## 6.2.2 Decomposition

Normally the primary ettringite formation in concrete occurs predominantly within the first hours of hydration. During this time the pH value of the pore solution depends on the amount of instantly soluble alkalis and therefore is still set at about 13.0 within the first hour [41]. Only with ongoing hydration the increase of the OH<sup>-</sup>-ion concentration continues due to the consumption of the solution phase. With it the question arises whether the primary formed ettringite remains stable under the changed pH-conditions of the surrounding solution phase.

The tests show that the ettringite precipitated in the solution becomes increasingly unstable with the following increase of the pH value of the solution due to addition of KOH. The ettringite becomes less stable the higher the pH-value becomes. Ettringite starts to slowly decompose at OH<sup>-</sup>-ion concentrations of 400 and 500 mmol/l. At higher ion-concentrations this process intensifies and in turn the sulfate-free reaction products monocarbonate and portlandite forms under the influence of CO<sub>2</sub> (fig. 14). Sulfate can be established in increasing amounts in the solution phase. Furthermore according to [32], the sulfate concentration arising in the solution increases with increasing concentrations of alkali hydroxides in the solution. The decomposition of ettringite occurs as long as the ion concentration arising in the liquid phase reaches the equilibrium with the solid materials. With this a dependence arises between the ettringite decomposition and the amount of the solution phase.

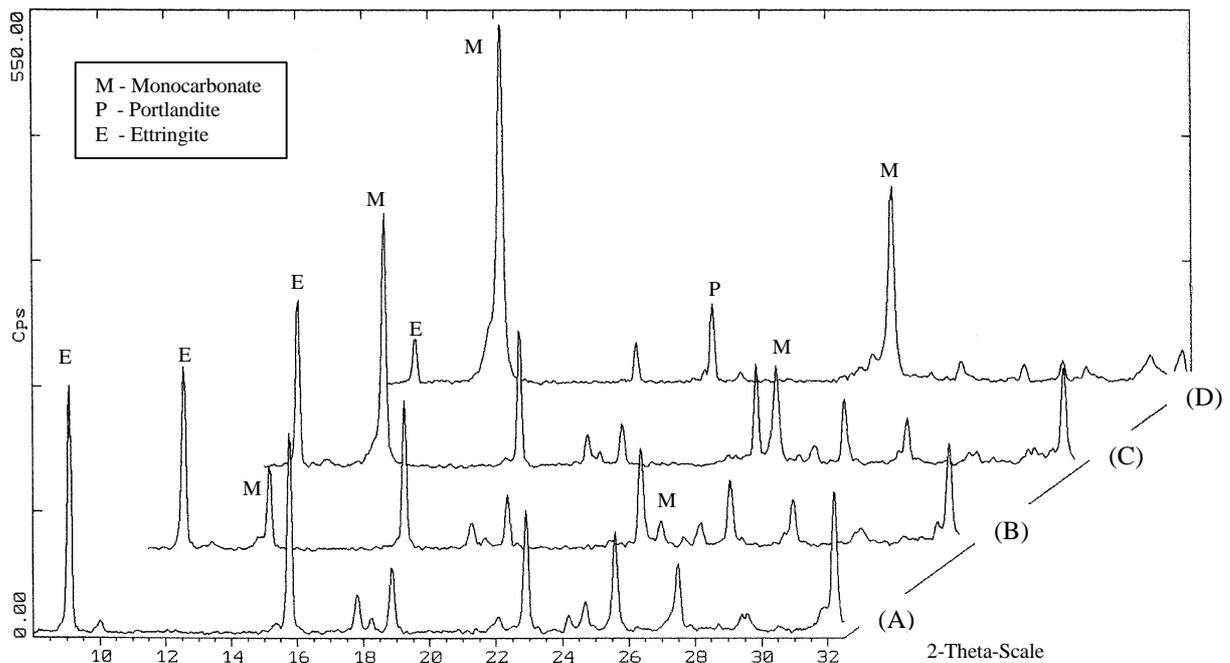


Fig. 14: X-ray analyses of ettringite and of the crystalline decomposition products at different alkali hydroxide contents in the solution phase:

- (A) - initial sample - KOH free (all peaks E);
- (B) - KOH = 410 mmol/l (all peaks E; exception - 2 peaks M);
- (C) - KOH = 550 mmol/l (all peaks E; exception - 2 peaks M);
- (D) - KOH = 770 mmol/l (all peaks E; exception - 2 peaks M, 1 peak P)

Further investigations in which already carefully dried synthetic ettringite was exposed to a KOH-solution with a mass ratio of 1:25 proved true the decomposition processes of the ettringite in the alkaline environment. Ettringite was completely decomposed within 3 days at an OH<sup>-</sup>-concentration of 770 mmol/l with predominantly monocarbonate and calcite and small amounts of aragonite and vaterite; gypsum and syngenite were formed as crystalline end-products (Abb. 15). Once again, it is to assume that sulfate-free calcium aluminate hydrate

phases or monosulfate and portlandite will be formed under  $\text{CO}_2$ -free conditions, which would be available for a reformation of ettringite.

With this it cannot be excluded that the ettringite primary formed in the hardened cement paste will be transformed into low-sulfate compounds at increasing pH values due to the hydration progress, whereby the sulfate appears partly in the solution phase.

### 6.2.3 Re-crystallization

During the utilization due to external and internal influences a decrease of the  $\text{OH}^-$ -concentration is possible mainly in pre-damaged concrete. Due to this fact pH-conditions can arise again under which ettringite could exist. As already mentioned the reaction partner sulfate necessary for the ettringite re-crystallization from the low-sulfate components also remains in the structure after leaching processes, so that a re-crystallization can occur.

The tests carried out with carefully dried synthetic ettringite also showed these results. After this ettringite was completely decomposed due to the addition of  $\text{KOH}$ , it essentially re-crystallized at pH value reduction due to dilution effects (addition of water). Small amounts of calcite and monocarbonate still remain (fig. 15). It is to assume that a complete re-crystallization is possible under  $\text{CO}_2$ -free conditions.

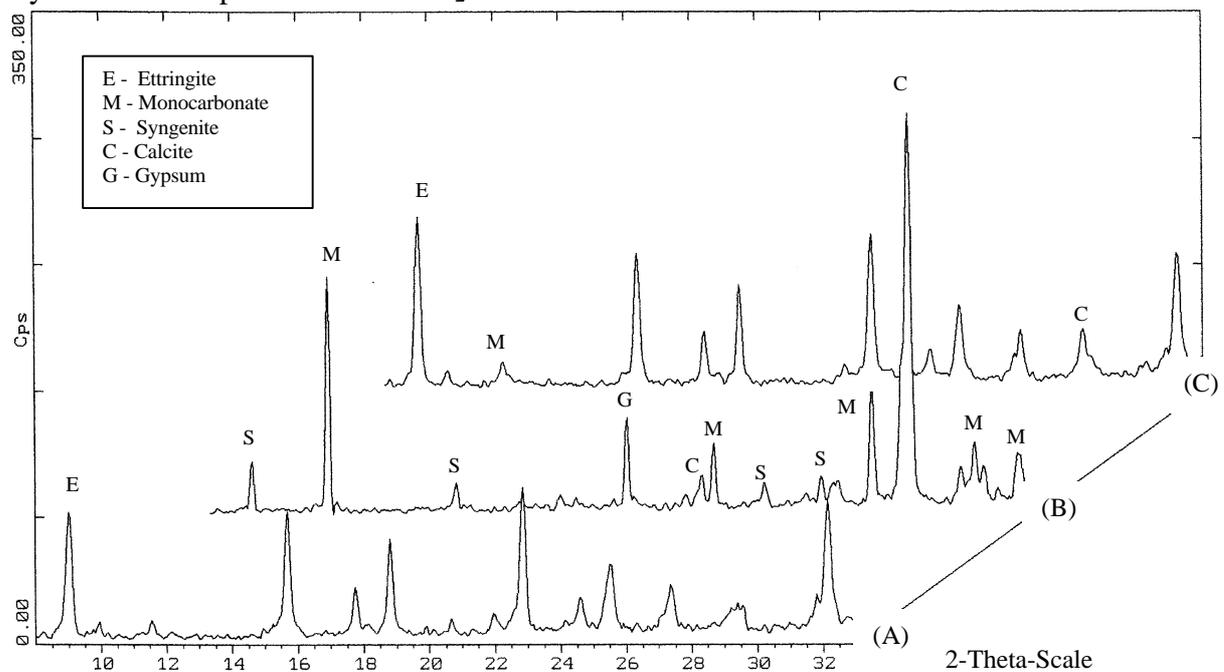


Fig. 15: X-ray-analyses from the following:  
 (A) ettringite (all peaks E)  
 (B) its crystalline decomposition products arisen in the solution phase at high contents on alkali hydroxid  
 (C) ettringite re-crystallized at reduced pH values  
 (all peaks E; exception - 1 peak M, 1 peak C)

The occurrence of larger amounts of ettringite mainly in porous, cracked or ASR-damaged concretes can therefore be attributed to a re-crystallization of ettringite which occurred due to the changed pH-conditions.

### 6.3 Consequences for the ettringite formation in hardened concrete

An application of the results from the investigations on the pore solution and of the investigations on the stability of synthetic ettringite in alkaline model solutions onto the real-system concrete makes clear that in sound concrete with ongoing hydration development pH values often exist in the solution phase under which the primary formed ettringite can not be stable. While primary ettringite formation can occur at pH values which are set around 13.0 using ordinary portland cements with an average alkali content, the pH value increases due to ongoing hydration up to 13.6 already after one day and above 13.8 after 28 days. Under this condition independent from risen temperatures, a decomposition of ettringite is possible so that ettringite can no longer be detected in the structure.

The quick attainment of a high degree of hydration due to heat treatment reduces the content of the solution phase in a short time so that the process of the pH value increases in the solution phase may be accelerated. Due to this fact, the decomposition processes of ettringite and the risen sulfate contents in the pore solution after a heat treatment which are often described may be attributed to the instability of ettringite at high pH values and less to its instability at higher temperatures. Due to changes in the liquid phase in mortar or concrete during the utilization and with its decreasing pH value, a re-crystallization of ettringite is possible mainly in pores, phase transition zones, and mature parts of the micro structure. Frequent changes in moisture or a permanent water supply as well as high permeability of the microstructure and structural damages accelerate the process of leaching alkalies and promote the ettringite re-crystallization, so that ettringite is detectable in conspicuous amounts in most damaged concretes.

### 7. Ettringite formation in air voids

Despite of the chemical processes already described (additional formation of ettringite from monosulfate), the accumulation of ettringite in the air voids - e.g. in pavement concretes (fig. 16) - can lead to physical damage of the concrete microstructure during freeze-thaw attack.



Fig. 16: Air void completely filled with ettringite crystals in a damaged pavement concrete

Due to the fine needle-like structure of the new phases formed in the air voids which normally interrupt the capillary transport, water absorption can be increased (fig. 17) so that not only a substantially greater quantity of moisture is present in the concrete during a freeze-thaw

attack, but also the room for expansion which was originally available has been restricted by the formation of new phases.

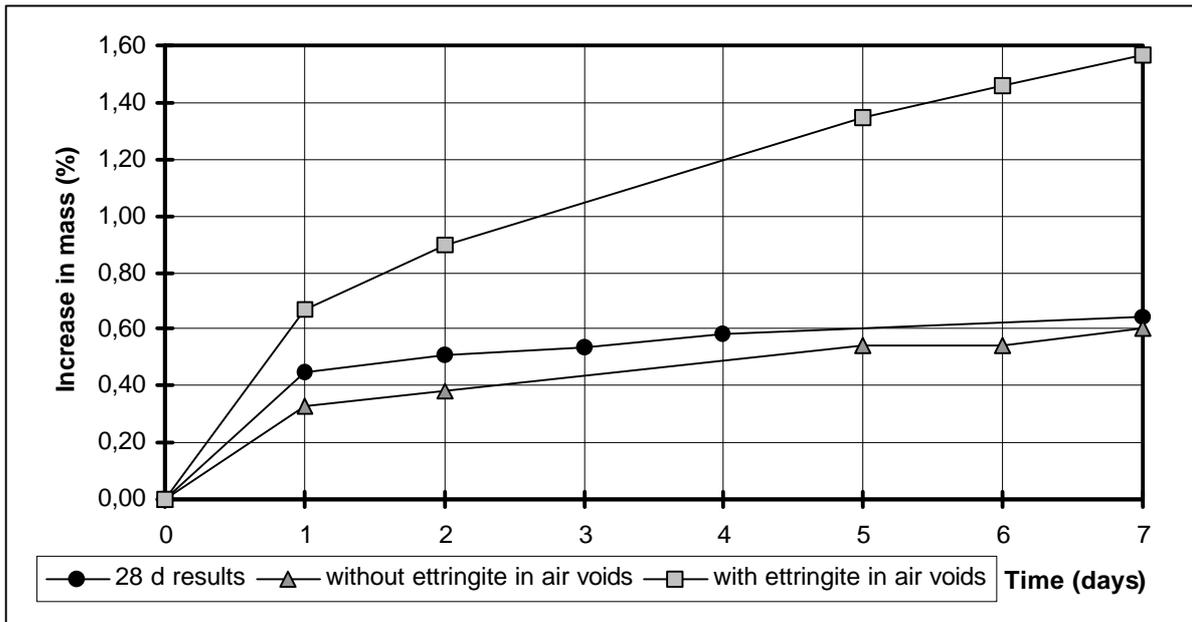


Fig. 17: Capillary suction (NaCl solution) of a pavement concrete after 28 d and with and without ettringite in air voids (after a laboratory treatment)

The air voids are no longer available for adequate compensation of the increase in volume which occurs during freezing as a result of the formation of ice (Stark and Bollmann [19, 20], Ouyang and Lane [67]). While with all previous investigations into frost/de-icing salt resistance of concrete (CDF test) no correlation between capillary suction and frost/de-icing salt resistance was found, in case of overgrown air voids, a strong increase in the amount of scaling occurs (Fig. 18).

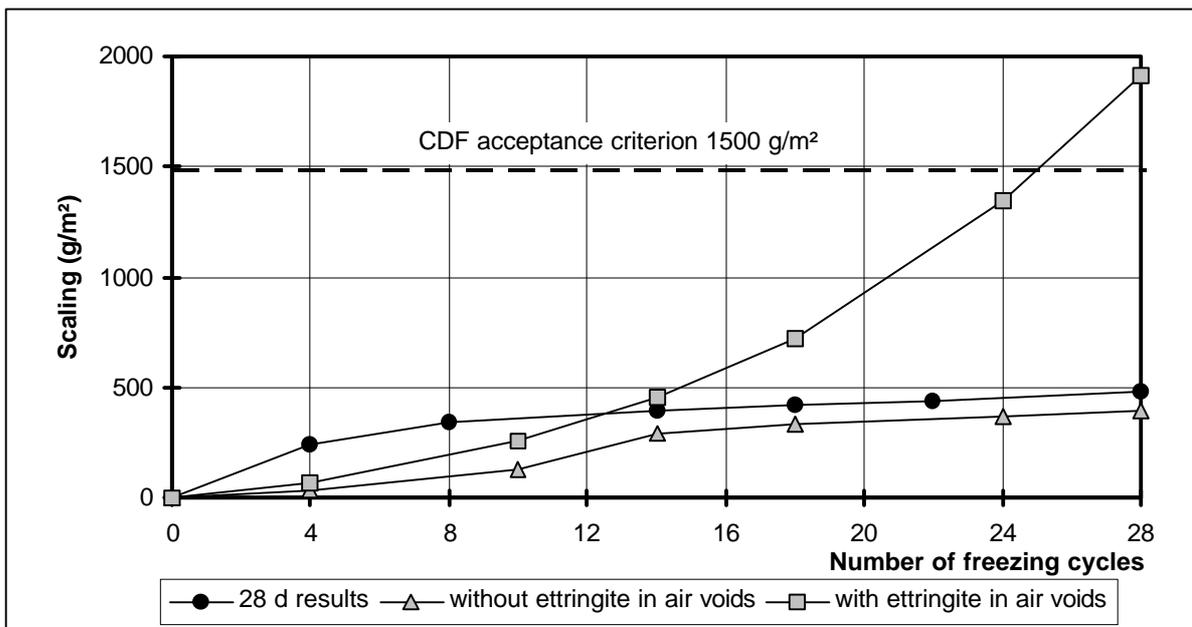


Fig. 18: Scaling curves (CDF test) of a pavement concrete after 28 days and with and without ettringite in air voids (after a laboratory treatment)

Caused by frost and de-icing salt attack, an internal damage of the concrete microstructure was also detected using the ultrasonic measurement method. Since after the CDF test the

transfer behaviour of the microstructure has deteriorated, a strong damping of the ultrasonic signal is recorded in the frequency spectrum. As has been proven by this results, the new formation of ettringite in the hardened concrete can, in the end, imply physical effects on the frost/de-icing salt resistance of the concrete.

## 8. Possible damage mechanisms

The question as to whether and how the formation of ettringite in hardened concrete is involved in the damage mechanism is still in controversial discussion. Is it the cause of cracks or does it only take place preferentially in cracks which already exist?

From the different theories on ettringite formation in hardened concrete, described in literature, possible damage mechanisms can be derived as follows:

- The primary ettringite formation during the initial hydration does not lead to damage, because this ettringite formation occurs in the plastic matrix and thus no stresses will be produced.
- If the ettringite formed primarily or delayed inside the microstructure is **micro-crystalline**, than in hardened concrete it may develop an **expansion pressure due to adsorption of water**, which can cause damages if the tensile strength of the microstructure is exceeded.
- Ettringite formed in the hardened concrete structure from less-sulfate containing compounds either **delayed** (due to higher temperatures during the initial hydration) or **additionally** (due to internal sulfate sources - e.g. through the affect of frost-, frost-deicing salt, through carbonation, from the clinker) may due to the **crystal growth** or due to the **increase in volume** cause stresses which exceed the tensile strength of the structure and can therefore cause damages. (The transformation of monosulfate into ettringite, for example, causes a 2.3-times increase in volume.)
- The **recrystallization** of ettringite in the hardened structure, due to moisture changes and accumulation of reactants, may lead to structure damages because of the **crystallization pressure** and the **increase in volume**.

Up to now it is not definitely proven whether or not the crystallization pressure during the formation of ettringite or the expansive pressure caused by water adsorption on micro-crystalline ettringite can produce cracks in a concrete microstructure, previously considered intact. There are various arguments against the “crystallization pressure“ theory. As is also described in [23], certain conditions are necessary for the development of crystallization pressure during the precipitation of a phase from solution which are probably not present in the concrete for years. Another argument against the “crystallization pressure“ theory is that the width of the annular gap around the aggregate grain, and hence the thickness of the ettringite layer, is proportional to the size of the aggregate, which points to a homogeneous expansion of the matrix [23].

The question of a crack-causing ettringite formation should not be overrated because, as mentioned above, prior damage of the concrete microstructure associated with micro-cracking, for example, can have many causes and can never be definitely ruled out under normal conditions of production and use. However, the recrystallized ettringite in the prior present micro-cracks could lead to constraint of the deformation caused by moisture, temperature, and/or load.

There is controversy in the discussion whether expansion caused by the ettringite is the primary cause of the structure damage or the consequence of a predamage of the microstructure. While e.g. Heinz [45] assumes that the structure damage occurs due to the

growth of ettringite formations in the matrix, Scrivener and Taylor [68], Lawrence [69], Fu and Beaudoin [70, 71] assume that the structure damages occur due to other causes such as high heat treatment temperatures and shrinkage, for example, and thus form optimal conditions for ettringite formation there.

Such defects in the concrete microstructure can be caused during a heat treatment due to physical effects through insufficient short prestorages and/or too fast heating and cooling. During utilization cracks can occur due to static and constructiv causes as well as internal stresses (through temperature and moisture gradients, freeze-thaw cycles, corrosion of reinforcement, as well as through other damage reactions such as ASR). These microcracks exist in the matrix, and especially in the transition zone between hardened cement paste and aggregate. The interface between hardened cement paste and coarser aggregates is especially exposed because in this area with a thickness up to 50  $\mu\text{m}$  – in contrary to the matrix - a higher porosity and an accumulation of portlandite and ettringite is set.

The predamages in the concrete structure can have manifold causes and they cannot be excluded under common production and utilization conditions. Such defects for the present facilitate the access of water as transport medium and as reactant, therefore promoting lokal accumulations of ettringite because capillary transport processes are interrupted and the reactants transported in the pore solution are deposited in pores and crack rims. There they react, promoted by sufficient space. Due to this, predamages of the concrete structure can promote and accelerate the damage reaction so that all influences which can cause cracks can also promote the ettringite formation in the cracks. The ettringite crystallized in these places is often not seen as cause of the damage but only as consequence. Subsequently it can lead to a constraint of deformations caused by moisture, temperature, and/or stresses. Therefore the expansion is a direct consequence of the crack enlargement. For such a crack enlargement due to ettringitte formation, much less energy is needed compared to the energy needed for the formation of new cracks in concrete.

The present findings therefore lead to the conclusion that micro damages in the structure, in connection with moisture exposure, are the cause of transport processes within the microstructure and in the transfer with the surroundings. They promote changes in the composition of the pore solution and with it the conditions for a recrystallization of coarse-crystalline ettringite. Thus, microdamages are often the pre-condition and not the consequence of the ettringite formation in hardened concrete.

Following mechanisms were derived from the results of our investigations:

- With the common high pH-values in the matrix the primary formed ettringite is not detectable. A decrease of the pH-value is necessary for a recrystallization of ettringite in the hardened concrete, e.g. by leaching of alkalis or by other pH-reducing reactions such as ASR.
- Predamages existing in the microstructure promote subsequently, due to increased moisture and phase transport, in availability of internal sulfate sources the ettringite formation at these exposed places and cracks were enlarged.
- The ettringite recrystallized in the entrained air voids can indirectly lead to frost damages because the air voids lose its effectiveness regarding the frost-deicing salt resistance.
- It can not be excluded that ettringite is often not involved in the damage mechanism and thus only a consequence of the microstructure damage caused by other processes.

The ettringite formation can be restricted by latent hydraulic and/or pozzolanic additives which, combined with calcium (e.g. blast furnace slag, silica fume or fly ash from hard coal).

$\text{Ca(OH)}_2$  is then consumed with the formation of additional calcium silicate hydrate, reducing the pore volume and consolidating the microstructure, especially in the regions around the aggregates. This restricts the damage promoting transport of moisture and phase-forming components in the concrete [72,73].

## 9. Summary

Concrete damage in conjunction with the formation of ettringite in hardened concrete is the result of complex long-term processes in which the concrete composition, technological factors during concrete production, and the effects of the surroundings are important. With preventive measures it is therefore not sufficient to take into account only one influencing factor, such as the chemical composition of the cement. All factors which lead to disruption and damage of the microstructure can also promote the formation of ettringite in hardened concrete. The occurrence of large ettringite crystals in concrete cracks is, as a rule, only a consequence and rarely the cause of the cracks.

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