SULFATE ATTACK ON CONCRETE – MECHANISMS AND PREDICTION MODEL

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ABSTRACT: The attack of sulfate bearing water on cementitious materials contains a great destructive potential. While previous studies mainly described the encountered phenomena, this research project focuses on a quantitative description of the deterioration process with the intention to deduce a simplified analytical model to predict strength, deformation and crack behavior of concrete under sulfate attack.

An essential part of the analytical-numerical approach consists in the separate analysis of processes on the micro, meso and macro level. Describing the hardened cement paste as a heterogeneous continuum with dispersed pores, the resulting stresses and cracks due to ettringite formation are simulated using fracture mechanics. Further numerical models for concrete are developed, taking into account the influence of aggregates and corrosion front induced strain gradients on the concrete damage. Related experimental investigations deliver the necessary characteristic values and provide also a basis for the validation of the model. The derivation of a simplified analytical prediction model for sulfate attack and its consequences on concrete complete the research study.

Such a model can aid substantially in the design and construction of concrete members exposed to sulfate attack and help forecasting the service life of members under such actions. It is a key part of an overall service life design, which will be a part of future code generations.

1 INTRODUCTION

The attack of sulfate bearing water on cementitious materials has a great destructive potential which can result in a complete destruction of structural members. The origin of the sulfates can be soils rich of gypsum, industrial waste waters or sulfate or sulfide containing aggregates. Depending on the accompanying ion of the sulfate anion, different corrosion mechanisms occur:

- H₂SO₄: dissolving and expansive attack
- CaSO₄ and alkali sulfates: expansive attack
- (NH)₄SO₄ and MgSO₄: exchange mechanisms of metal ions of salt with C-S-H and expansive attack of sulfate

In the past 20 years, different imaging methods contributed to clarify the basic principle of the degradation mechanism considering the processes in the pore volume and the change of phases. Sulfate ions ingress in the pore volume of the hardened cement paste due to capillary suction and diffusion and react with AFm-phases forming ettringite. Thus, the volumetric expansion results in the degradation of the cement paste microstructure. The macroscopic damage pattern is characterized by strains in the material along with crack formation on the surface, where gypsum crusts can be found when high concentrations of sulfate ions are present in the solute [Her99]. With increasing proportions of aluminates in the AFm-phase, rising tensile strains evolve, whereas according to the literature only marginal volumetric expansions can be measured when ferrous ettringite is formed.
While previous studies mainly described the encountered phenomena, this research project focuses on a quantitative description of the deterioration process with the intention to deduce a simplified analytical model to predict strength, deformation and cracking characteristics, i.e. the durability behavior of concrete under sulfate attack.

2 NUMERICAL INVESTIGATIONS

The numerical analyses are based on a finite element model of the deterioration process in the hardened cement paste and concrete respectively using statistical fracture mechanics. This model takes into account as key parameters primarily sulfate intensity, type and duration of the attack, porosity, the material composition and geometry. An essential part of the approach consists in the separate analysis of processes on the micro, meso and macro level. In this consecutive analysis the results of the lower level will be integrated into the homogenized model of the next higher level.

So far two consecutive numerical models have been developed, describing the processes on micro level (modeling of hardened cement paste) and meso level (modeling of aggregates, matrix and interfacial transition zone). The calculations are carried out using the finite element code DIANA.

2.1 Numerical model on the micro level

2.1.1 Model geometry and pore size interval

The pore radii of hardened cement paste range from 10 nm to 1 mm. However, the modeling of pores within more than one order of magnitude in one model is not reasonable for geometric reasons. Thus, to cover the whole spectrum of relevant pore radii, multiple calculations with consecutive pore radius magnitudes are needed. For each model, the calculated material behavior is used as input data for the material properties of the finite element model of the next higher order.

According to Skalny et al. [Ska02], pores in the range of several micrometers and smaller are highly responsible for the generation of cracks due to ettringite formation (heavy sulfate damages as a consequence of ettringite formation were observed although the latter could not be detected using scanning electron microscopy, which accounts for the formation of almost amorph ettringite structures in very small pores). Thus, the modeling of the hardened cement paste was started with a pore size interval from 100 nm to 1000 nm. Within this range, four pore size classes with similar class width were defined, using a logarithmic scale. The particular number of pores of one class was calculated from the differential pore volume of the hardened cement paste (CEM I cement, age 7 days, w/c ratio = 0.65). The principle of this approach and the distribution of pores are illustrated in Figure 2.1 and Table 2.1 respectively.
Fig. 2.1. Left: Differential pore volume of different hardened cement pastes; the modeled range of pores is marked in grey (measured with mercury intrusion porosimetry). Right: Definition of four pore size classes with pores ranging from 100 to 1000 nm.

Table 2.1. Number of pores in individual class, range from 100 to 100 nm according to Figure 2.1 considering an area of 20 µm square.

<table>
<thead>
<tr>
<th>pore size class</th>
<th>radius ri [nm]</th>
<th>area of single pore [10^{-14} \text{ m}^2]</th>
<th>area percentage [%]</th>
<th>number of pores</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>750</td>
<td>176,7</td>
<td>0,363</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>420</td>
<td>56,0</td>
<td>0,823</td>
<td>6</td>
</tr>
<tr>
<td>C</td>
<td>240</td>
<td>17,7</td>
<td>1,680</td>
<td>38</td>
</tr>
<tr>
<td>D</td>
<td>130</td>
<td>5,6</td>
<td>2,340</td>
<td>168</td>
</tr>
</tbody>
</table>

The statistical distribution of the pores in the model is assured by the use of a random number generator calculating the x- and y-coordinates of each pore centre. The biggest pores are calculated first, followed by the pores of the next smaller class until the smallest class in the end. In order to avoid too small spacing between pores or even overlapping, a concluding plausibility check with defined minimum values is carried out. Pores with interspaces below these values are finally eliminated. In the automated geometry generation the above generated data file of pore distribution is implemented in DIANA applying a FORTRAN routine.

2.1.2 Mesh generation

In the finite element model rectangular elements of second order are used, because triangular elements tend to stress locking and excessive stiffness. As mesh generation in DIANA is done geometry-based (the geometry is generated first and meshing is done afterwards, starting from the edges), complex geometries with highly curved boundaries may induce problems in the automatic meshing routine if rectangular elements are used. Thus, heavily irregular meshes or program termination may result.

In order to solve this problem, different approaches were tested whereof the idea of geometry segmentation proved to be most effective.

Since this method still results in highly irregular meshes even with very small elements, additional auxiliary square boxes around the pores were introduced. These are generated as cut-outs around the pores within the routine of automatic pore generation. Hence, a separate mesh generation of the overall area with cut-outs and the cut-outs with pores themselves is possible.
This technique now allows a nearly fully automated mesh generation in combination with a high mesh quality. The only disadvantage is the increased required space for the square boxes compared to the circular pores, causing the need of a more strict plausibility control with respect to interspaces and overlapping of pores.

The effectiveness of this technique is illustrated in Figure 2.2, showing the differences in mesh geometry with and without applied auxiliary boxes. Figure 2.3 depicts the overall model with an edge length of 20 µm, composed of 18 single segments.

Fig. 2.2. Segment without (left) and with (right) auxiliary square boxes.

Fig. 2.3. Finite element mesh of hardened cement paste containing circular pores within a pore size interval of $10^{-7}$ to $10^{-6}$ m and consisting of approx. 18000 elements.

2.1.3 Material properties of hardened cement paste

The constitutive behavior of the hardened cement paste was modeled using the “Crack Band Model” developed by Bazant and Oh (see Figure 2.4) in order to facilitate the imaging of increasing crack formation and propagation. Within the numerical simulations the different cohesive crack models such as Total Strain Rotating Crack, Total Strain Fixed Crack as well as Smeared Crack were investigated.
Furthermore, the heterogeneity of material properties was taken into account by a Gaussian distribution of the material parameters (particularly tension strength and fracture energy, see Figure 2.5). Therefore, material classes were defined and allocated randomly to the individual elements (Monte Carlo Method).

According to Powers and Taylor [Tay90], the values for the strength and stiffness of the hardened cement paste without pores (hcp0) were set to $f_{hcp0,c} = 240 \text{ MPa}$, $f_{hcp0,t} = 24 \text{ MPa}$ and $E_{hcp0} = 30 000 \text{ MPa}$. However, reliable magnitudes for the fracture energy of the mere matrix without pores could not be found. Hence, the fracture behavior was modeled according to the concrete behavior given in CEB Model Code 90 (see Figure 2.4). It was assumed that the strains $\varepsilon_{cr1}$ and $\varepsilon_{cr}$ correspond to crack widths of $w_{c1} = 1 \text{ nm}$ and $w_c = 10 \text{ nm}$.

### 2.1.4 Modeling of sulfate attack

The propagation of the corrosion front was characterized in a first approach with the simplified empiric relation according to Atkinson and Hearne [Atk84] whereas the corresponding pore stresses were estimated using the formula for linear crystallization pressure $p$:

$$ p = \frac{R \cdot T}{\nu} \cdot \ln \left( \frac{c}{c_s} \right) $$

(2.1)

with $R$ as the ideal gas constant, $T$ as temperature, $\nu$ as molar volume of crystalline substance, $c$ as actual concentration of the solute and $c_s$ as saturation concentration.

Assuming that ions not involved ($K^+$, $Na^+$, $OH^-$ and others) do not have any influence on the solubility of sulfate, and ettringite, monosulfate as well as portlandit are given as solid phases, a value of $p = 31 \text{ MPa}$ was calculated ($T = 20 \°C$) [Fen10].

According to Gollop and Taylor [Gol92], the thickness of the ettringite formation zone was set equal to 200 $\mu$m. To further minimize the extent of numerical calculations with DIANA, the course of crystallization pressure over time was approximated with a bilinear function [Fen09].

### 2.1.5 Results of numerical investigations

Applying the derived model above, numerous calculations were carried out to study the influence of different parameters and to verify the suitability of the model. Within these studies, simulations using the overall geometry, single segments as well as segment groups were conducted. The main problems in the finite element computations were numerical instabilities with increasing crack propagation as well as excessive calculation time using the overall model. The most important results are detailed below:

- The existing model constitutes a functional approach to describe the degradation process in hardened cement paste subjected to sulfate attack.
- A crack formation along crack paths can be reproduced with the model. The implemented heterogeneous material behavior has a positive influence on the formation of distinct crack paths (see Figure 2.6).
- Considering the three cohesive models Total Strain Rotating Crack, Total Strain Fixed Crack and Smeared Crack, the Smeared Crack Model turned out to be the most suitable due to its significantly higher numerical stability and lower calculation costs.
High calculation times are a core problem for models with more than 1000 to 1500 elements. Lowering of the stipulated convergence criteria causes only limited reduction of calculation costs but the convergence is improved.

Against one's expectations, increasing mesh refinement did not have significant influence on convergence. Partly, numerical instabilities occurred even earlier.

Considering the applied iteration schemes (Newton-Raphson, modified Newton-Raphson, Constant Stiffness), the regular Newton-Raphson method together with a preceding line search scheme showed the best results.

Fig. 2.6. Critical crack strain $\varepsilon_{cr}$ along a crack band for a segment of the overall model subjected to crystallization pressure in pores.

2.2 Numerical investigations on the meso level

Parallel to the investigations on the material behavior of hardened cement paste on the micro level, calculations on the meso level were carried out. The concrete was modeled as a three-phase-system consisting of aggregates, mortar matrix and interfacial transition zone.

2.2.1 Geometrical model

Similar to the proceeding on the micro level concerning the distribution of pores, the aggregates with a maximum size of 8 mm (grading curve B8 of DIN 1045) were divided into four sub-classes sized 8, 4, 2 and 1 mm and statistically distributed using the above mentioned FORTRAN routine. In a first step a square shaped $40 \times 40 \text{ mm}^2$ model was used which was reduced to $20 \times 20 \text{ mm}^2$ later on due to high calculation times. The material behavior of the aggregates was assumed to be linear elastic with an elastic modulus of $E = 50000 \text{ MPa}$ having no limiting tensile stress.

The mortar matrix was reproduced using the approach of the heterogeneous continuum with variation of strength and stiffness values (see chapter 2.1). Mean values for strength and elastic modulus were adapted for the recomputation of given experiments with magnitudes at the time 0 (start of sulfate attack) from 45 to 65 MPa (compressive strength) and 30000 to 36000 MPa (elastic modulus), respectively. In order to facilitate crack formation, the cohesive crack model approach was applied, similar to the investigations on the micro level.

The interfacial transition zone between aggregate and matrix was taken into account by the implementation of an intermediate layer of elements. To start with, its thickness was set to 40 $\mu$m, independent from the aggregate diameter. However, the adaptation of the thickness of the transition zone to the corresponding aggregate size is easily possible and can be implemented in future calculations. The elastic modulus of the interfacial transition zone was coupled to the elastic modulus of the matrix elements with reduced values of 60% [Yan03].
2.2.2 Modeling of sulfate attack

The sulfate-induced expansion process was modeled via a volumetric expansion of the mortar matrix. Thus, measured volumetric strain values of mortar samples were specified in the model by applying a temporally and locally variant temperature field to the matrix with a linear correlation between temperature and measured strain values.

Furthermore, the decrease of the mortar strength and stiffness observed in experimental studies was taken into account by a variation of the model parameters over time. The corresponding values were adapted not only for the matrix but also for the interfacial transition zone in intervals of 30 days [Fen10].

2.2.3 Recalculation of experiments and parameter studies

In order to verify the suitability of the deduced numerical concrete model, the experimentally measured deformation behavior and the compressive strength of concrete samples were recalculated with DIANA for a period of 90 days and 120 days respectively. The essential material properties of the matrix were calibrated on mortar samples from the same test series. The calculated strains of two concretes with different types of cement (CEM I and II) were in good agreement with the measured values (Figure 2.7) and the calculated compressive strengths could reproduce the right tendencies. Thus, the deduced model is basically capable of calculating the degradation process in concrete subjected to sulfate attack in a realistic way.

![Graph showing linear expansion](image)

**Fig. 2.7.** Linear expansion of two different concretes subjected to sulfate attack. Comparison of experimental and numerical results.

The influence of the different material parameters and geometry effects on the overall results was examined in various parameter studies. Details can be found in [Fen09].

3 EXPERIMENTAL INVESTIGATIONS

The experimental investigations provide the basis to determine the deformation behavior and the mechanical properties of hardened cement paste subjected to sulfate attack. The obtained results constitute a reference for the calibration of the numerical continuum model and provide the essential values for linear expansion, mass change, flexural strength and compressive strength as well as porosity (total porosity, pore distribution).
The prismatic samples are sized 100x40x10 mm$^3$. Amongst the tested parameters are the water-cement ratio, the age at testing as well as the type and duration of storage (Table 3.1).

Table 3.1. Overview on tested parameters of experimental program.

<table>
<thead>
<tr>
<th>water-cement ratio (T = 20 °C)</th>
<th>type of storage</th>
<th>duration of storage ^1/age at testing [d]</th>
<th>number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4 and 0.6</td>
<td>sealed</td>
<td>0, 7, 28, 90, 365</td>
<td>2·5·3 = 30</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>7, 28, 90, 365</td>
<td>2·4·3 = 24</td>
</tr>
<tr>
<td></td>
<td>solute I</td>
<td>7, 28, 90, 365</td>
<td>2·4·5 = 40</td>
</tr>
<tr>
<td></td>
<td>solute II</td>
<td>7, 28, 90, 365</td>
<td>2·4·5 = 40</td>
</tr>
<tr>
<td>total number of samples:</td>
<td></td>
<td></td>
<td>134</td>
</tr>
</tbody>
</table>

\^1 after start of examinations at the age of 3 months

For the first 3 months all samples are cured the same way. After stripping at the age of 7 days, the samples are stored over water in a covered tray with constant temperature. After 90 days one part of the samples is left sealed in the conditioning chamber whereas all other samples are immersed in either water or sodium sulfate solution with two different sulfate concentrations (Na$_2$SO$_4$ solution with high and low concentration, see Table 3.1 “solute I” and “solute II”). The samples stored under water are required to specify the volumetric expansion and the difference in strength between sealed and water stored samples, respectively. Together with the sealed samples they serve as a reference and will contribute to a better understanding and interpretation of the test results gained from the samples subjected to sulfate attack.

The sealed reference samples are tested at the age of 3 months, corresponding to a duration of storage of 0 days according to Table 3.1. Afterwards all samples are tested 7, 28, 90 and 365 days after the beginning of their individual storage condition. The number of samples related to the different storage conditions is given in Table 3.1. Altogether 134 samples are tested.

4 Overview on Research Modules and Prediction Models

The configuration of the model and the interaction of the different modules are shown in Figure 4.1. The numerical model on the micro level is calibrated with measured material properties and damages of hardened cement paste samples. Combined chemical and mineralogical investigations deliver the necessary transport coefficients and volumetric expansions whereas the crystallization pressures have to be calculated on the basis of thermodynamic data, because they cannot be measured directly [Fen10].

In the next step, the calculated expansions and material deteriorations of different micro level models (which consist of hardened cement paste without pores and the pores themselves) are averaged and thus provide the input data for the matrix on the meso level, which is modeled as a heterogeneous continuum. Together with the aggregates and the interfacial transition zone a three-phase model on the meso level is obtained. The experiments on mortar and concrete are used to calibrate and verify the model on the meso level.

Because of the various influencing parameters in the three-phase model, their effects and importance are investigated in numerous parameter studies. The derivation of an appropriate material law for concrete and a simplified analytical prediction model for sulfate attack on concrete members complete the research study.
5 CONCLUSION AND OUTLOOK

Within the research study numerical models on the micro and the meso level could be developed that are suitable to describe the qualitative deterioration processes of concrete subjected to sulfate attack. There is still some effort required to improve the reliability of the calculations and to get a better knowledge of the relevant processes and characteristic parameters on micro level.

Further research study is necessary to derive a simplified analytical prediction model for sulfate attack on concrete members. Such a model can substantially aid in the design and construction of concrete members exposed to sulfate attack and help forecasting the service life of members under such actions. It is a key part of an overall service life design, which will be a part of future code generations.

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