Concept of the evaluation of corrosion by acid and sulphate solution of cement based materials[1]

Introduction Durability is the capability of a building, assembly, component, structure or product to maintain minimum performance over a specified time under the influence of degradation factors. The durability design of concrete structures is based on implicit rules for materials, material compositions, working condition rules for materials, structural dimension, etc. Example of such rules are minimum concrete cover, maximum water/cement ratio, and minimum cement content. Modern building codes make use of a reliability theory based on probabilistic approach. Increasingly, these approaches expand into durability design. For example, Corr et. al presented an empirical reliability analysis for sulfate attack on concrete [1] and Gehlen and Schießl [2, 3] presented a probabilistic design concept of carbonation of concrete. This kind of concept optimizes the cost for construction, maintenance, and repair while considering safety factors.

The aim of this study is to present a probabilistic concept of the evaluation of durability. This study concentrates on corrosion by acid and corrosion by sulphate solution.

A Designer must be able to prove the fulfilment of certain requirements, referring to serviceability limit state and ultimate limit state. For these purposes two models are required. Frist a deterministic model showing the degradation over time as a function of an appropriate design parameter is needed. Design parameters e.g. environmental factors and properties of the building materials vary greatly. Because of this the performance of a structure must be treated stochastically. This means that not only the average values, but also distributions must be taken into account. For these purposes a second probabilistic model is needed. These models must give reliable information on the deterioration process, because of this the model must be validated. With the aid of these models the designer can make decisions on the required dimensions e.g. concrete cover and type of material e.g. water to cement ratio and cement type. To choose between different materials a contingent of data records as input parameters for the two models is needed. These data records

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must be available for different concrete and mortar compositions.

In the following these particular topics are discussed and at the end an example for the concept of the evaluation of corrosion of cement based materials is presented.

Deterministic model The deterministic model Transreac uses, which simulates corrosion effects of building materials caused by the attack of chemical solutions was developed by Schmidt-Döhl [4, 5, 6]. This model combines the calculation of chemical reactions with the calculation of transportation processes within the structure. The calculation of chemical reactions is based on a repeated determination of the stable phase assemblage (Gibbs energy minimization, Pitzer model, consideration of chemical kinetics). The transportation module covers a lot of different transportation processes within porous materials. In addition modules for the calculation of corrosion effects were implemented. These corrosion effects include the expansion caused by the formation of ettringite, the loss of material strength and the loss of mass caused by the dissolution of phases. A lot of improvements were made since the papers [4, 5, 6] . The accuracy and speed of the thermodynamic algorithm was increased and the simulation of redox-reactions was incorporated. All transportation processes can now be calculated as 2-D processes. The heat and moisture transport can be now calculated on the basis of the model of Künzel [7]. It is also possible to calculate flow by seepage pressure. Additionally the model for the transportation caused by diffusion potential was improved.

With this highly flexible model a lot of different simulations were done in the past. The examined materials cover cement mortar, concrete (also with fly ash and blastfurnace slag), sandstone and sorel cement. The aggressive solutions cover sulfate solutions, chloride solutions, acid, seepage water from a landfill, saline solutions characteristic for salt mines and solutions with different content of aggresive carbon dioxide (see for example [5, 8, 9, 10, 11, 12]).

Probabilistic model Transreac was extended to a probabilistic model. This was accomplished by incorporating the deterministic model into a Monte Carlo simulation. The Monte Carlo method is a stochastic technique, meaning that it is based on the use of random numbers and probability statistics to investigate problems (see [13]). This numerical technique was used to preserve all the features and the full flexibility of the deterministic model. This extension made the calculation of the probability of failure and sensitivity analysis possible. Both of them are important for the safety concept.

Both of these models must be validated. For this purpose a certain amount of corrosion experiments from literature are used. The corrosion experiments taken into account deal with corrosion of concrete, mortar or cement stone by

- nitric acid,
- hydrochlorid acid,
- sulphuric acid,
- aqueous ammonium solution,
- and sulphate solution.

Most of the simulated data are consistent with the experimental derived data. An example is presented below. The validation of the probabilistic model will be demonstrated by a corrosion experiment. The experiment is described in [6]. Mortar specimens with a length of 100 mm were in contact with sodium sulphate solution (44 g/L). The formation of ettringite and the induced strain were investigated. Fig. I shows the ettringite profile and the strain of the mortar after 303 days in contact with the sulphate solution.

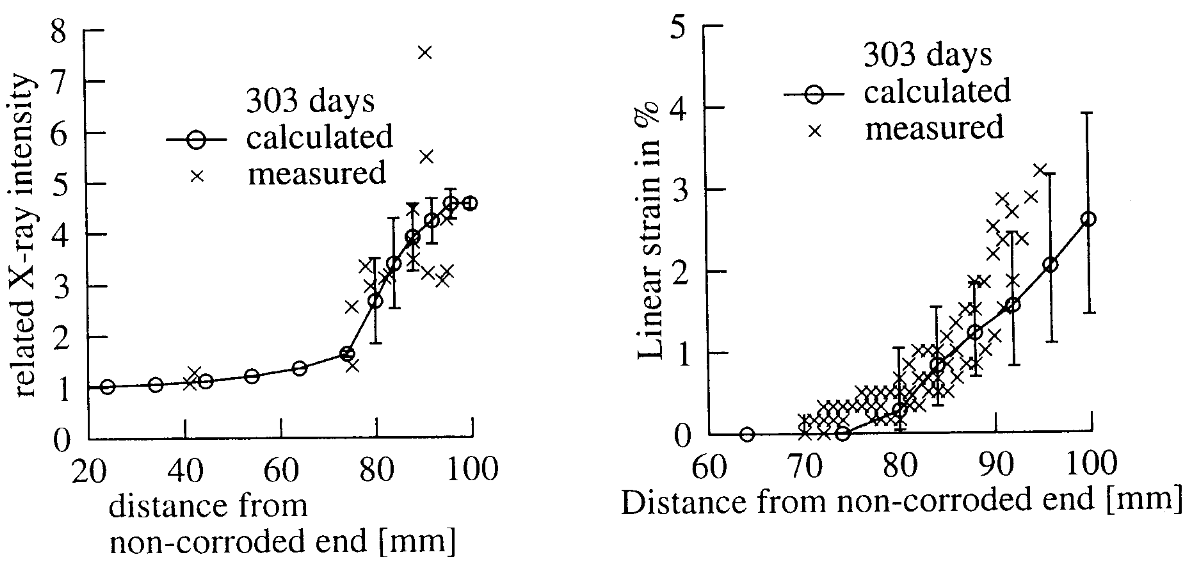

Fig. I.: Ettringite profile and the induced strain of corroded specimen after after 303 days in contact with 44 g/L Na_2SO_4-solution (see [6]).

The calculated results are consistent with the experimental data (see Fig. 1). The error bars are the results of the Monte Carlo simulation. They show the standard deviation of the simulated ettringite profile. The Monte Carlo simulation shows an increased standard deviation beginning at 75 mm from the non corroded end of the specimen. This can also be found in the experimental results. Most of the experimentally derived scatter of the ettringite concentration can be predicted by the Monte Carlo simulation. Only the simulated scatter at 90 mm from the uncorreded end of the specimen is too small. The experimentally derived linear strain and their scatter match the simulated data. These excellent results show that the deterministic model (Transreac) in combination with a Monte Carlo simulation is a powerful tool to set up the probabilistic safety concept of durability problems.

Data records To use the probabilistic and the deterministic model it is essential to provide a lot of data that deals with the average values and also the distributions of properties of building materials. For this purpose an extensive database is provided in this work. The database contains about 9500 values on:

- porosity (e.g. pore distribution, bulk density)
- data to calculate transportation process (e.g. capillary suction, diffusion)
- mechanical data (tensile strain)

This data is available for concrete, mortar and cement stone for different water to cement ratios and different cement types. The data sets were extracted by assembling data from about one hundred publications. The data was analysed by a special stochastic procedure. Most data from the literature shows a strong deviation even on the same material. One example of this phenomenon is shown in fig. II.

This deviation can be explained by different experimental methods of estimation of diffusion coefficients, different treatment of the samples, or inhomogeneous material. For the use of the safety concept the deviation is only allowed if it can be attributed to inhomogeneous material. To overcome this problem, future data measurements should be more standardized. Furthermore, data to calculate chemical reaction must be provided, this is also presented in this work.

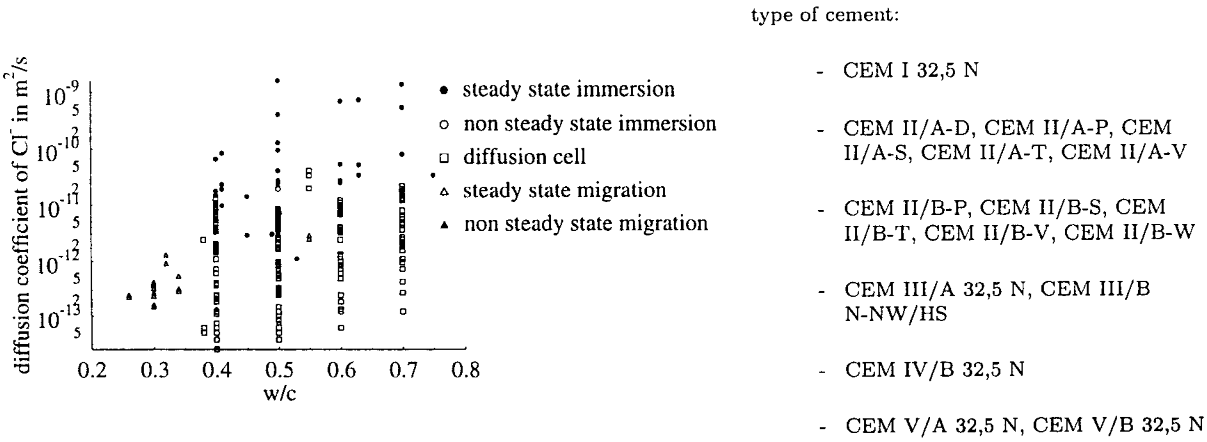

Fig. II.: Diffusion coefficient of Cl^- for concrete at various water to cement ratio. Diffusion coefficients are from the following sources: [14] [15] [16] [17] [18] [19] [20] [21] [22] [23] [24] [25].

Example for concept of the evaluation of corrosion on cement based materials Structures must be reliable with respect to their life time. In the mathematical sense reliability is the probability of the structure to resist environmental influences. The probability of failure, which is the complementary value to the probability of reliability, is the commonly used value. The acceptability of low residual risk and a small probability of failure give the possibility to consider economic aspects within the design of buildings. First, to calculate the probability of failure for each attack the limit state must be defined. This means the mechanism of corrosion must be considered. Then with the aid of the deterministic and probabilistic model the probability of failure with respect to the life time is calculated. The calculated probability of failure must be lower than the maximum allowable probability of failure. When setting the maximum allowable probability of failure for serviceability limit state, relative cost of safety measure and exposure classes is taken into account like described in Rackwitz [26]. This concept is present for different aggressive environmental conditions:

- sulphate solution
- acid solution
- ammonium solution

In the following example a concept for the evaluation of durability is demonstrated. In Fig. III the probability of failure as a function of time of exposure in 2.1% Na_2SO_4 is shown. The graph on the left shows the results for mortar made with ordinary portland cement and the graph on the right shows the results for mortar with slag cement. Additionally the maximum allowable probability of failure is marked.

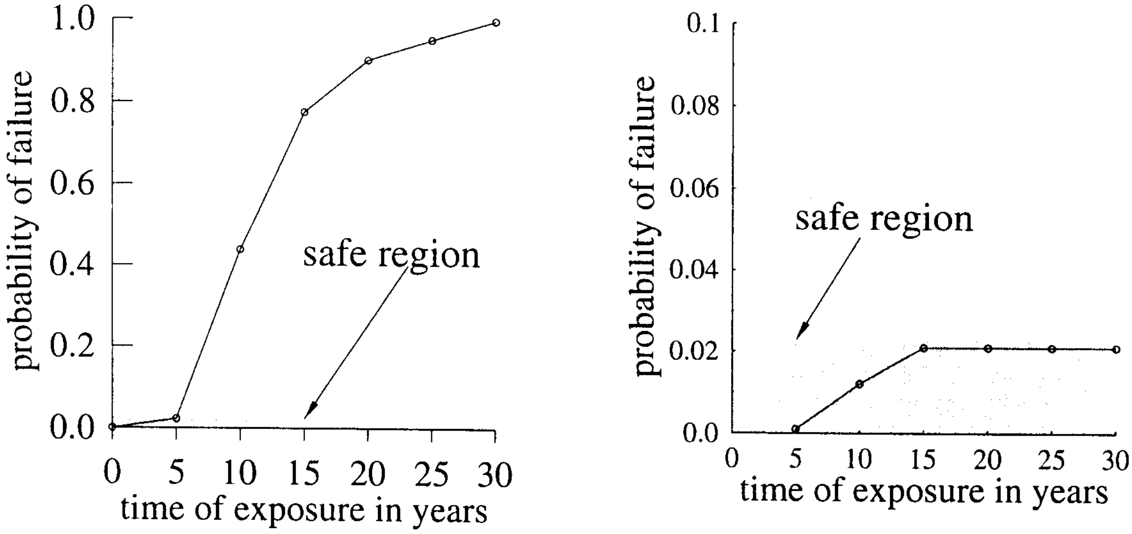

Fig. III.: Probability of failure as a function of time of exposure in 2.1% Na_2SO_4 solution for mortar made with portland cement (left) and for mortar made with slag cement.

The results of the Monte Carlo simulation show that the Portland cement based specimens are in the safe region for up to 5 years. On the other hand the slag cement based mortar is reliable during its life time. This is in agreement with the practical guidelines which specify that this type of portland cement is not suitable for the production of concrete or mortar with high resistance against sulphate attack. On the other hand slag cement is suitable. Additionally a sensitivity analysis was performed. Sensitivity factors provide information of the importance of several initial values on the simulated corrosion effect.

Summary This work presented a concept of the evaluation of durability. The work deals with corrosion induced by sulphate solution and chemical degradation by a leaching process. The concept is based on a probabilistic approach and was accomplished by the combination of the transport-reaction model Transreac with a Monte Carlo simulation. This concept include an extensive database. The necessary validation of used simulation models were demonstrated. Finally the application of this concept is demonstrated by certain examples which deals with corrosion of cement based materials in sulphate, acid, and ammonium solution.