Model for the Hydration and Formation of Structure in Cement Paste

Abstract. A simulation model for the hydration and formation of microstructure in cement paste is presented. The model renders a three-dimensional description of the porous space and its development during hydration. The formulation of the hydration process is based upon the constitutive volumetric approach of Powers and Brownyard. The hydration was described by coupled sub-processes. This processes are the solution of non-reacted cement, the transport of this material and the formation of products in the capillary pore space. It was implemented by means of finite elements method. The porous structure is presented by the simulation model as a local porosity distribution which includes a more detailed information on the capillary pore space than given by existing models. Taking the results of mercury intrusion porosimetry into account the local porosity distributions can be transformed into distributions of cylindrical capillary pores. By help of this procedure a state description depending on the hydration time is given for an advanced modelling of the materials behaviour starting at the scale of microstructure.

Introduction. Many chemical reactions, transport and damage processes take place within the capillary pore space. The pore space and its structure have a decisive influence on material behaviour. Transport and damage models used to describe the behaviour of a material during its lifetime often have to start from a simplified status description at the beginning of its lifetime. With a more precise description of the material status, it will be possible to predict the behaviour and durability of the material under actual-use conditions more accurately. The pore space is formed during the hydration phase. Initial condition, and hardening conditions and processes are factors that influence both hydration and pore-space formation and structure. With the models available today for these hydration and structuring processes it is not possible to adequately describe the relevant capillary pore space. This paper proposes a model that allows hydration and structuring processes to be considered as a closely linked phenomenon and to represent the capillary pore space within a wide range of pore radiuses.

Model basis. The model starts on the basis of the volumetric model of cement hydration proposed by Powers and Brownyard. Instead of considering the hardening reactions of the Portland cement clinker in detail, a simplified overall balance is drawn up, which only relates to the model phases non-hydrated cement, water and resultant product, while the mineralogical composition of the cement is only considered in a smeared manner. The water is not bound, or it is chemically or physically bound in the products as hydration progresses. This approach provides the mass and volume balance of the hydration model.

Hydration model. In the cement paste, hydration takes place in three sub-processes. The cement is dissolved on the surface of the non-hydrated cement particle. In its stead inner products of a gel-porous structure form. The dissolved cement moves with the concentration gradient into the free pore space, which is where another sub-process takes place: the formation of the outer products. These sub-processes cannot be considered independently. In the model describing the condition variables 'concentration of the dissolved cement' and 'structure of the pore space', these sub-processes are linked.

The transport process is formulated as a diffusion process on the basis of the Fourier differential equation. The dissolution of the non-hydrated cement increases the concentration and is considered to be a source. The formation of product reduces the amount of available dissolved non-hydrated cement, and is hence considered to be a sink. The formation of products reduces the porosity, and the pore space is increasingly filled with products. This has a very direct influence on the transport and product formation processes. Changes in the transport process have an effect on the concentration and thus, indirectly, on the dissolution process and also on the product formation process.

For practical application, the finite-element method is used. The effectiveness of the three sub-processes is adjusted with the aid of model parameters. These parameters are determined in an adaptation calculation, i.e. by comparing the measured and the calculated hydration rate. The analytical model is applied with the aid of a three-dimensional representative volume element (RVE). The RVE contains the cement paste with the components water and spherical cement particles. The number of particles and their diameter are determined on the basis of particle size distribution, water/cement ratio and RVE size. As a first step, the particles are distributed in the RVE at random. As a second step, an agglomeration process is considered. Under normal conditions (e.g. no superplasticizers), van-der-Waals attraction forces favour the formation of particle clusters in the cement paste. In the simplified analytical model, the particles are moved along resultant forces between neighbouring particles. This restructuring process simulates flocculation. This distribution describes the condition in the cement paste much more accurately than a random distribution. After that, the RVE is discretized into individual cubic elements. This discretization is about 1 µmedge length at an RVE edge length of 100 µm. No clear distinction is made into solids and pore space. The individual elements may at the

same time contain parts of non-hydrated cement, pore space, and (at a later stage) also products. The RVE now describes the initial status of commencing hydration. This is the point at which the FEM-based hydration model starts. The cement dissolves, is transported and forms products in the empty pore space.

Local porosity distribution representation of the structure. The result of the simulation calculation is a three-dimensional local porosity distribution as a function of time. In this local porosity distribution, porosity characteristics are assigned to individual elements but no element-specific binary distinction is made into solids or pore volume. Therefore additional information is available on the structure. In this respect, the model differs from the way distribution is represented in other available models. Two widely used models are CEMHYD3D [5] and HYMOSTRUC [15]. The cellular CEMHYD3D automaton is more detailed in the hydration reaction, but it classifies the volume elements (voxels) very clearly into solids or pores. This is why this model cannot supply any information on structure below the resolution used in the calculation (approx. 1 µm). The HYMOSTRUC model is a hard-core soft-shell model, in which the outer products are shown as compact shells. The model proposed here differs in its much more realistic representation with diffuse outer capillary product layers in the local porosity distributions.

The computed local porosity distribution cannot directly be compared with measured results. The necessary analytical methods and the processes for data preparation have as yet not been fully developed or such methods and processes are not available at all. This is another reason why the model parameters have to be calibrated indirectly, using the degree of hydration as a function of time.

Transformed representation of the structure. For some advanced models and the intended comparison with results obtained with mercury intrusion porosimetry (MIP), representation of the capillary pore space that assumes the pores to be cylinder pores offers certain advantages. It is, for instance, easier to start from cylinder pores for the description of transport processes in more advanced models. The calculated local porosity distributions can be transformed into local pore radius distributions. They can then also be used for comparison with measured values. The idea underlying transformation is to assign a pore spectrum to the different element porosities, which is specific to this particular porosity. Unfortunately, a direct approach (for instance a geometric approach) is not available for this assignment. The assignment of the (porosity-) specific radius spectra is derived from measured data. This implies that the transformation process is calibrated on the basis of MIP measurements. MIP is often used as a method for determination of the pore radius distribution in macroscopic samples. This method supplies information on a wide spectrum of radiuses, but there are some uncertainties that follow from sample preparation and the measuring method used. The result is, in particular, influenced by the

effect of ink-bottle pores, which is due to the three-dimensional pore arrangement. Large pore radiuses can often only be identified by a smaller intrusion radius, and their volumes are thus not correctly represented in the pore spectrum. In how far the pores are identified can be determined by approximation with information obtained in a structural analysis from the calculated RVE. This information will partly correct the distortion produced by ink-bottle pores. Since this additional information on the porosity distribution is only available on the element level, the compensation is only an approximate compensation and is limited to large pore radiuses.

Transformation now also makes porosity-specific radius spectra available, in addition to local porosity distributions. On this basis, radius distributions can be determined cumulatively for the hardened cement paste, approximatively corrected by the effect of ink-bottle pores. Effects that originate in the measuring process (MIP) and sample preparation cannot be eliminated. With transformation calibration, these effects enter the computed result.

Extension and application. As a first extension, the model was applied to hardening under sealed conditions. Since the free water becomes bound in the course of hydration, the hydrated cement is subject to a self-drying process. Pore desiccation starts with the large pore radiuses. To calculate the radiuses, the transformation process that has been calibrated before is used in the model. In the desiccated pores, the hydration sub-processes come to a standstill. These pores can, therefore, not be filled with hydration products, and fairly large interconnected capillary regions with large pore radiuses remain.

In another application, the formation of the microstructure was analytically simulated in the interfacial transition zone (ITZ) between aggregate and hardened cement paste. For this purpose, the wall effect in the ITZ was considered with an adjusted particle arrangement. Because of this effect, the ITZ is characterized by a high porosity right at the start of the hardening phase. Results show that this zone is not completely filled with product throughout the entire hydration phase. In particular under sealed conditions, the porosity in the ITZ has to be expected to by high, since the larger pores are because of the self-drying effect desiccated during the hydration phase already. The ITZ, which is determined by factors such as the water/cement ratio, can be effective for several micrometres. Calculations have identified the ITZ to be a week point, and this has been confirmed under real conditions.

Summary and perspectives. The proposed model allows a large part of the capillary porosity in the hardened cement paste, which has a decisive influence on the material behaviour, to be shown as a three-dimensional structure. Starting from the cement paste, the structure is calculated regarding the hydration process and the hardening conditions (moisture saturation, temperature).

The calculation combines three model processes: cement dissolution, diffusion-induced transport of the dissolved cement in the pore space, and product formation in the free pore space. The calculations made are transferred to a discrete lattice by means of the FEM. The model is called HydraFE as a abbreviation for the modelling of the hydration process by means of the finite-element-method.

The first discrete analytical result is a spatial porosity distribution. Although this distribution is linked to the dissolution of the FE lattice, it makes no clear distinction into solids or pore space. This is why individual elements differing in porosity and phase composition are possible.

In a second computation process, the three-dimensional porosity distribution can be used to calculate the distribution of radiuses. For this purpose, the spatial porosity distribution is transformed into an equally spatial radius distribution. Radius distributions can thus also be determined from the porosity of individual elements or from larger pore structures.

This work is intended as a contribution to a virtual laboratory for building material research and development. In particular the measuring instrumentation required to determine and describe the multi-scale pore structure is a field requiring additional development work. It would also be desirable to develop a realistic and generally applicable microstructure model. This model should, on the one hand, be available without restrictions for additional models developed on its basis and it should, on the other hand, permit validations on the structure level, which is at the moment not possible at all or only with certain reservations.