MICRO-HYDRATION, PORE CONNECTIVITY AND DURABILITY OF CEMENTITIOUS MATERIALS

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Abstract
Latest developments in Hymostruc enable the possibility to evaluate the pore connectivity of an evolving microstructure while also considering the contribution of the ITZ and air voids and to examine the influence on frost durability. The numerical model is used to visualize this phenomenon and to show the contribution of both the pores and the ITZs to the continuation of capillary pore. Once the capillary pores are blocked by ongoing hydration the transport of harmful dilutions are restricted to move into the microstructure. However, distinction is made between the pore connectivity as developed in the bulk paste and the connectivity as developed by connected ITZs. A blockage of the capillary pores (pore discontinuity) as well as a blockage of the ITZs contribute to an increased depercolation of the cementitious microstructure and improve the microstructural performance. The surface durability of freeze/thaw resistance of pavements and chloride ingress is evaluated in view of the pore continuity modelling approach.

1. INTRODUCTION
The issue of modelling the pore connectivity in an evolving cementitious microstructure has been studied by authors before, i.e. [1,2]. It is considered as a way to examine the mechanism that contributes to assess the durability of concrete surfaces exposed to deleterious species [1]. With the evolution of the microstructure during hydration a network of capillary pores is created that can act as a kind of internal “infrastructure” through which harmful species can be transported and that can damage the inner quality and performance from the interior. The main parameters that play a role in this respect are those parameters that affect the formation of the capillary pore space and that enable the development of a transport network. In this respect, besides the bulk capillary pores also other “sources” may contribute such as the ITZ, and in case of pavements also the air voids may contribute and become part of the internal transport network. The big question is how these different elements of the network contribute to the connectivity and in which respect they contribute to the durability
and service life performance of a cementitious material. In this paper, therefore, the Hymostruc model is used to assess the contribution of these elements in terms of connectivity and permeability. The model enables the possibility to evaluate the contributions quantitatively and an attempt is done to quantify the critical values for those parameters that determine the durability of concrete, and, especially, for pavements.

2. MICRO-HYDRATION

Micro-hydration is considered to be the hydration of cement grains at the micro-scale level. Hydration at this level includes the growth of the outer CSH gel and the inner CSH gel which are the basic elements that account for the load bearing capacity of a concrete. During hydration the pore space will reduce and the space will be occupied by the CSH gel formation. The microstructure also includes the capillary pore water and can be simulated with numerical simulations models. In this paper, the numerical model Hymostruc is applied which is a model that can be used to simulate the development of an evolving virtual microstructure of cementitious materials [4,5]. The model is a full 3D model and calculates the development of the microstructure as a function of the particle size distribution, the water-cement ratio, the chemical composition and the temperature of the mix for Portland and blended cements [6]. The processes that run during the pozzolanic reaction can be distinguished into different classes, i.e. morphological, physical, chemical and thermodynamical. In terms of the development of the cementitious microstructure, all classes have their own particular characteristics and affect the pozzolanic reaction in a certain way. In Hymostruc, these interactions and inter-particle relations that exhibit during evolvement of these processes are modeled explicitly. Within the model Portland cement is the primary basis for hydration modeling. However, recently the model has been extended in order to simulate the hydration of blended (slag, silica fume or filler) cements.

The particle structure of the cementitious material forms the initial state of the microstructure. An envelope shape has to be defined and complies with periodic boundaries. This approach enables filling of the envelope shape while accurately complying with the imposed water/cement ratio. Particles are stacked in this envelope shape based on random selection of locations while first placing the larges particles followed by the smaller particles following the particle size distribution. After having placed all particles, the initial state of the 3D microstructure has been realized and can be used for calculation of the hydration process (see Fig.1). From the 3D particle structure, as provided in Fig. 1, the inter-particle spacing’s and the paste density can be calculated for each particle individually. Based on this information, the distance between the hydrating particles are known and can be used for the simulation of the particle growth. In Hymostruc the hydration of the individual particles is modeled explicitly in two different ways, e.g. following a statistically-based cell concept and according to a full 3D approach. While the cell concept is based on an elementary paste volume that contains the volume of water and the volume of (blended) cement grains up to a certain fraction, the full 3D approach calculates the inter-particle distances directly from the generated 3D particle structure. The cell concept is the approach that was initially proposed by Van Breugel [4]. In this approach, the expansion of the hydrating particles is considered to grow both in inward direction (Inner CSH gel or High density CSH gel)
Figure 1: Example of a 3D virtual microstructure (wcr 0.4, Blaine 400 kg/m²) consisting of cement particles with air bubbles (a) and isolated air bubbles (b) at initial state, and microstructure (c) and capillary state of water (d) after 1000 hours of hydration.

and in outward direction (Outer CSH gel or Low density CSH gel). According to the cell concept, the growth of the hydration products, representing the inner and outer CSH gel, are similar for each individual fraction. The outer expansion of the hydrating particles is calculated according to the so-called particle expansion mechanism (Fig 2) [4]. The expansion mechanism describes the outer growth of a spherical central particle \( x \), while accounting for the embedding and (partly) hydrating cement and/or pozzolanic particles captured in the shell of the expanding central particle, and where the embedded particles are smaller than the central particle. The potential outer growth volume available for the particle expansion may be calculated from a mass balance concept. Based on this concept a relation was derived between the chemical composition of the silicate reactions and morphology of the CSH gel.

Figure 2: Schematic impression of the particle expansion mechanism with addition of pozzolans or air voids [4,5].

Similar approach can also be followed for the expanding pozzolanic particles. Following this, a relation has been realized between the chemical nature of the cementitious system and the potential expansion of the grains in a developing microstructure, i.e. a relation between the type of cementitious material, the morphology and initial state of the microstructure.
3. **PORE CONNECTIVITY**

Assessing the connectivity of the microstructure can be conducted with the Hymostruc model by means of evaluating the virtual microstructure (Fig 1). The model uses the expanded particle model for cement hydration as provided in Fig 1 while applying a 3D voxelization (digitizing). With this, the model is divided into voxels (3D pixels) for a given resolution, which is user defined. Fig 3 shows the sensitivity of the microstructure towards the resolution of the voxelization. The figure a) shows the 2D front view of the 3D microstructure at a resolution of 1 pixel per µm and figure b) shows the same 2D front view at a resolution of 3 pixels per µm. It indicates the sensitivity of the modeling approach towards the resolution. When turning all the hydration products into white, the capillary pore structure will remain. This image is the basis for the 3D connectivity assessment of the capillary pores. The black and white colors at a given resolution form the structure that can be evaluated for its pore connectivity. The digitized 3D structure of the capillary pores looks like a special binary structure and can be evaluated with the pore connectivity model where each black voxel being part of the capillary pore structure is identified and evaluated upon its position in the system and how it is connected to its neighboring voxels, i.e. it borders either to another “pore voxel” or to a “solid phase voxel”. The model enables the possibility to calculate the change of the connected voxels, representing the capillary pore space, as a function of the degree of hydration. With increasing degree of hydration, i.e. the densification of the microstructure due to the development of the hydration products, the relative volume of the connected capillary pores, will decrease. The connectivity model, therefore, has to consider each particle individually in a stepwise changing sequential process. In order to handle this, the flood fill method has been implemented. Flood fill, also called seed fill, is an algorithm that determines the area connected to a given node in a multi-dimensional array [5]. The flood fill algorithm takes three parameters: a start node, a target color, and a replacement color. The algorithm looks for all nodes in the array which are connected to the start node by a path of the target color. There are many ways in which the flood-fill algorithm can be structured, but they all make use of a queue or stack data structure, explicitly or implicitly. With this algorithm, in a 3D structure the neighbors can be found in a 6 direction configuration or in a 26 directions configuration (incl. corners in 3D). The difference is whether the voxels situated at the

![Figure 3: Digitized 2D front view of the 3D microstructure with a) resolution 1 pixel per µm, b) 3 pixels per µm, and c) the inverse state used for the connectivity analysis.](image-url)
outer corners of a central voxels are also considered as neighbors. In Hymostruc both methods are implemented for a 2D and 3D model. In Fig 4, the principle of connectivity searching is shown for a 2D situation. For this 2D pattern, a 4 or 8 direction configuration can be chosen with the difference that the neighbors at the corners are not considered connected for the 4 directions configuration and for the 8 direction they are considered to be connected as well. In Fig 4 the 4 direction configuration is shown where only the upper right corner and the lower left corner can be connected. The algorithm will not trace the other quadrants as connected since the corners are not considered to be connected in this particular case.

Figure 4: Left: Flood fill method principle [7]. Right: Connectivity calculated from 3D microstructure (bulk paste) for 1, 2 and 3 pixels per µm (ppm) and for three different water cement ratios (wcr) after 28 days of hardening.

In the 3D capillary pore structure calculated with Hymostruc the 6 or 26 directions configuration can be selected. Both may give slightly different results, but, at the cost of significant differences in computation time. In order to evaluate the sensitiveness of the calculated connectivity towards the voxel resolution of a virtual microstructure, this issue has been scrutinized in more detail. The question now is, however, how this resolution affects the connectivity of the capillary pore structure calculated over the full depth of the 3D microstructure. This has been examined by calculating the connectivity of a microstructure by applying the three different resolutions. In Fig 4 (right), the results of this calculation are provided as a function of the actual capillary pore volume. From the results it can be observed that the pore connectivity, representing the actual pore volume over the initial pore volume, is decreasing with decreasing capillary pore volume. The resolution only shows little influence on the results and show equal tendency. In order to show the dependency of the pore connectivity with changing the water cement ratio the results for a wcr of 0.35 and 0.45 are also included in the figure and show a slightly different tendency of the pore connectivity.

4. ITZ

The Interfacial Transition Zone is the zone that surrounds special bodies in the paste and creates a wall-effect. In this respect the aggregates, but also the entrained air bubbles cause an ITZ which has properties that differ from the bulk paste properties. Especially in terms of the
connectivity of the capillary pore system, ITZ-zones show significant different behaviour. The connectivity of a capillary pore system has been analysed in more detail for a ribbon microstructure (rib 100 µm), while emphasizing the connectivity over three different thicknesses of the ITZ starting from the outer surface, i.e. 0 - 5 µm, 0 – 10 µm and 0 – 20 µm, relative to the connectivity of the bulk paste, i.e. 20 - 80 µm, and is provided in Figure 5. The figure shows large differences in the pore connectivity for the ITZ regions relative to the bulk paste indicating the different roles of these elements in an internal capillary transport system.

5. AIR VOIDS

Introducing air voids into a mixture turned out to reduce the probability on salt scaling due to low temperature cycles and frost. Besides, air voids also contribute to the development of a capillary network inside a concrete mixture. One of the main issues in this respect is the average (travel) distance in between the air voids (chord length). This distance, together with the prevailing permeability may determine the ability and the ease at which moisture can move through a hardening and hardened concrete. The first question, therefore, is about the distribution of the air voids in a concrete as a function of the percentage of air added to the mixture. Recently, at the University of Michigan, Hansen et.al [3] conducted preliminary research on the average air void spacing for different percentages of air entrained in mortars. In Figure 6, a distribution function is provided where data is shown for a 3% air inclusion. The figure represents the normalized chord length frequency versus the chord length which is representing the average surface to surface distance spanning two air bubbles. From the data received from this experimental work a Rosin Ramler distribution function $G(x)$ (see [4]) has been fitted. Good agreement could be reached and this distribution function representing the average distribution of the surface to surface distance of air voids could, therefore, also be used in the simulation model. In order to get more insight into the average travel distance of moisture in between the microstructure and how this could contribute to the total movement of moisture through a microstructure, this distribution function has been implemented in Hymostruc. The idea was to examine the relationship between the shortest surface to surface
distance as a function of the percentage of air voids intruded in the paste. For this analysis the 3D Hymostruc module is used where cement particles and air voids are stacked in space randomly. A module has been implemented enabling the calculation of the distribution function for the shortest distance between two air voids of the same diameter in a paste matrix (Figure 6). The figure gives a good impression of the percentage of air entrained in a paste and the effect on the distance to a nearest particle. This information can be used to calculate the potential contribution of air bubbles in the internal capillary transport system. However, this also depends on the permeability of the paste.

6. DURABILITY

Durability in view of the connectivity of capillary pores is a way to assess microstructural damage of cementitious materials from the interior. The potential to transport harmful dilutions through the interior of a microstructure is important for all concrete structures. Elements that contribute to the creation of an “infrastructure” are the capillary pore system themselves, but also the ITZ and air voids/air bubbles (pavements) may contribute to the ease at which species may move internally. The assessment of durability in this respect and the performance of it during service is depending on the rate at which the species may move through the pore structure. In particular the rate at which species can move through a capillary pore space depends on the permeability, which on its turn, depends on the pore morphology, which is unique for each mixture. The contribution of the ITZ may be significant since it offers the possibility for species to by-pass the bulk paste-capillary pores in dense microstructures so that the route to follow will be shorter and, therefore, also faster, and may affect their service life. Recently, in the Hymostruc model, a full 3D module has been implemented with which the transport of species through the capillary pore space of an evolving microstructure can be evaluated [8]. The model is still under development, but the first results are very promising as can be seen from Figure 6. The red parts show the high concentrations and the blue parts the low concentrations of species. This model can be used to optimize a microstructure for those durability problems were the state of moisture is decisive and control their service life.
7. CONCLUSIONS

The issue of connectivity of the capillary pore network is evolving for hardened concrete. It is of particular relevance for those conditions where concretes are exposed to harmful dilutions such as deicing salts and/or CO₂ or sulphates. In particular for pavements, the issue of pore connectivity is rather complex due to the combined contributions of capillary pore system, the ITZ and the effect of entrained air bubbles. The Hymostruc model with its graphical interface provides a quantitative and visual means of evaluating the different contributions of these elements, and how they affect the existence and development of harmful mechanisms that cause deterioration of the concrete surfaces. More research on the liquid transport properties is underway with the aim to develop a full microstructure-based model for service-life assessments and surface deterioration of concrete pavements.

REFERENCES

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