Morphological nature of diffusion in cement paste

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ABSTRACT: The diffusive transport in cement based materials plays a crucial role in the degradation process of concrete. Rapid development of numerical models has provided novel methods to investigate the influence of microstructure on the evolution of the properties of cement based materials. A virtual 3D porous microstructure created with available hydration models provides a fundamental basis for the analysis of the morphological influence onto the effective diffusion coefficient. Such an approach contributes to a better understanding of the phenomenology and thus improves the predicting reliability of the coupled transport models. This paper investigates the influence of the morphological effect onto the diffusion properties of hydrating cement pastes using the cement hydration and microstructure development model HYMOSTRUC3D. The diffusive properties of the simulated microstructures are analyzed employing a numerical 3D transport model. The modeling results are compared with available literature results.

1 INTRODUCTION

Transport in cementitious materials plays a crucial role in both the degradation process of building materials and the containing of hazardous wastes. A good quality of the concrete cover enhances the durability and reliability of concrete structures. For example, aggressive external ions such as chloride ions and sulphates penetrate into the concrete's cover causing corrosion of reinforcing steel in concrete and cracking due to expansion mechanisms. Thus, the increasing focus on the reliability aspects requires a better understanding of mass transport phenomenon through the evolving porous microstructure of cementitious materials. Modeling challenges include difficulties in the overall description of this multi-scale random porous medium characterised by a wide range of sizes, from nanometersized pores to centimeter-sized aggregates.

One parameter that is of paramount importance is the effective (macroscopic) transport coefficient. A relevant and reliable method is needed in order to obtain effective diffusion coefficient (D_{ef}) with an acceptable accuracy. Various experimental methods exist but they are either time consuming or have too many drawbacks. A representative starting point for analysis of transport properties in 3D cement based microstructure can be obtained either by: 1) simulation packages (e.g. CEMHYD3D, HYMOSTRUC, μ ic), or 2) experimentally, e.g. by micro tomography (Koster et al. 2006). Simulating a microstructure evolution during hydration is an advantageous (fundamental) starting point to model the morphological nature of the effective diffusion (transport) coefficient. A virtual 3D microstructure created with an available hydration models provides a basis for the analysis of the morphological influence, including the porosity, tortuosity, constrictivity and the pore water content effect onto the effective diffusion coefficient. Such an approach contributes to a better understanding of the phenomenology and thus improves the predicting reliability of the coupled transport models.

The steady state transport analysis by solving Laplace equation is an established method for obtaining the macroscopic effective transport coefficient of porous materials (Garboczi 1998, Koster et al. 2006). An electric analogy approach is based on Ohms law which is equivalent to the steady state mass flux equation, diffusion as well as Darcy's law (see later chapter 2.3). The capillary porosity is assigned an ionic conductivity value as in aqueous solution (G_0), while cement particles have zero conductivity since they contain no porosity. Fast (e.g. conjugate gradient relaxation) algorithm solves the complete steady state problem of the concentration distribution in a random material across which a concentration difference is applied (Fig 1). The output of the algorithm is the concentration at every node, from which the total fluxes and thus effective transport coefficient is calculated.

There are two main network approaches which may be employed, here termed as: 1) direct, and 2) indirect. In direct approach each pixel in the 3D microstructure is mapped directly into a node in either a finite element (FE) or finite difference (FD) analysis (Garboczi 1998). The indirect approach simplifies the pore structure by constructing a pore network of mostly larger pore elements (e.g. cylinders) that reduces the computational costs (Koster et al. 2006). However, the advantage of the direct method is that the calculation is done on a simulated microstructure directly as digitalized, preserving the original morphology of the pore network.

Garboczi (1998) implemented FE and FD codes in Fortran for calculating steady state effective transport coefficients. Zhang et al. (2011) estimated the effective diffusion by using finite element commercial software using adiabatic boundaries (no fluxes) on the side surfaces (Fig 1). Garboczi (1998) implemented periodic boundary conditions in his FE and FD codes by creating a shell of imaginary extra nodes around the main system. Periodic boundary conditions (p.b.c.) are physically more realistic. Furthermore, p.b.c. implementation enables to use smaller representative elementary volumes and hence to improve system resolution with negligible impact on computational cost. In literature 3D numerical methods for effective transport calculation are manly focused on the mass transfer governed solely by one process (e.g. diffusion or permeability). Thereby, chemical reactions (i.e. ion/solid interactions) of the diffusing ions and the water movement is not considered. However, the modeling techniques outlined by numerical algorithms can be extended to consider further these effects. Therefore, the goal of this project was to develop a flexible and efficient code within original Hymostruc platform that could be easily used for further developments. A finite difference (FD) program is written in C++ programing language



Figure 1. a) 3D simulated microstructure, b) Steady state flux across *z*-axis (depth), with periodic or adiabatic boundary conditions employed on 4 side faces parallel to the imposed flux.

for solving steady state transport problems on virtual 3D digital images generated by Hymostruc. The p.b.c. were implemented differently than in Garboczi's code (1998), i.e. without an addition of extra shell layers around the system. Hymostruc graphical interface was updated to visualize the transport simulation results.

2 THEORETICAL

2.1 *Morphological nature of transport in cement paste*

Effective diffusivity coefficient corresponds to the diffusion coefficient at the macroscopic scale, the pore liquid phase being at the microscopic scale. It is an geometrical factor accounting for the complexity of the shape of the porous system defined by its tortuosity, porosity and constrictivity. Relative diffusivity can be described as the ratio of the effective diffusivity (D_e) of an ion in the cement paste composite relative to its value when diffusing in bulk water (D_0) and ranges between 0 and 1. The relative diffusivity values computed for cement pastes are needed as an input into a multi-scale structural model for mortar or concrete to determine the effect of aggregates and their surrounding interfacial zones on the diffusivity of the structures.

2.2 Diffusion modeling

The diffusive transport of species in a fluid is described by the II Ficks law:

$$\frac{\partial u}{\partial t} = -\nabla \left(D_i \nabla u \right) \tag{1}$$

where *u* is he concentration of the diffusing species, D_j is the diffusivity in cement paste component j = pore, hydration products, or cement grain. At the macroscopic length scales, the diffusive transport is generally modeled as:

$$\partial u/\partial t = -D_{ef} \nabla^2 u \tag{2}$$

where u is the average concentration of the diffusing species, and D_{ef} is the effective macroscopic diffusivity in porous media.

2.3 Universality of transport laws

The calculation of the transport properties as described here can be viewed in a larger general aspect because of the analogy between the following four laws: Fourier's law for heat flow; Ohm's law for electric current ($I = G\nabla U$); Fick's law for diffusion ($J = -D\nabla c$, see later eq. (5)); and Darcy's law for liquid (and gas) flow in materials ($V = k\nabla p/\eta$). The universality in these laws is that the flux is

proportional to a driving force (difference in temperature, voltage, concentration or pressure) and inversely proportional to the resistance. An electric analogy approach may be used in calculation of the effective transport property. After obtaining the effective electrical conductivity (G) of the investigated random porous medium the desired effective property (e.g. diffusion coefficient, D or mass transfer coefficient, k) can be further calculated (Garboczi 1998, Koster et al. 2006). For example, the effective (macroscopic) diffusivity coefficient is then obtained by utilizing the Nernst-Einstein relation (Garboczi 1998, Koster et al. 2006) which states that the relative diffusivity (D_{ef}/D_0) is equivalent to the relative conductivity (G_{ef}/G_i) , where the relative diffusivity is the ratio of the effective diffusivity (D_{ef}) of an ion in the cement paste composite relative to its value when diffusing in bulk water (D_0) and ranges between 0 and 1:

$$D_{ef} / D_0 = G_{ef} / G_0 = J_{ef} / J_0$$
(3)

In a steady state condition, when the fluxes are steady in time, eq. (2) reduces to Laplace eq.:

$$D_i \nabla^2 u = 0 \tag{4}$$

The total steady state flux J_{ef} under uniform concentration gradient as driving force across the whole porous system in z direction is obtained by solving the Fick's first law:

$$J = -D_i \nabla u \tag{5}$$

The J_0 is the flux in homogenous system with all pores with same physical dimensions of the investigated system (*d*-depth, *w*-width and *h*-height represent number of voxels in *x*, *y*, and *z* direction, *N*-total number of voxels). Finally, the $D_{\rm ef}$ can be obtained easily from eq. (3).

3 IMPLEMENTATION

The procedure of numerical implementation of the model is depicted in Fig 2. First a virtual 3D microstructure output obtained by Hymostruc cement hydration simulation is discretized into a regular 3D mesh (lattice in Fig 3.). This is done by digitalization algorithm built-in a Hymostruc. Each voxel in a lattice is assigned to be capillary pore, cement grain or hydration product according to the position in the microstructure of the cement paste. The user can choose to calculate transport: 1) through capillary pores only; or 2) through capillary pores and hydration products (more precisely CSH gel, as detailed in 3.1). Then, for each shearing surfaces between neighboring voxels in x, y, and z directions



Figure 2. Flowchart of numerical implementation.

a connectivity coefficients are assigned (c_x, c_y) , and c_z respectively) and stored in three **c** vectors (whose lengths are the number of voxels in the system, N), Fig 2. Six neighbor connection was used, considering that the central node is connected only by sharing faces of cubes in x, y, and z directions. Considering additional connectivity through cube's corners and edges would increase neighbor connections to 26. Connectivity coefficients are obtained from microscopic transport properties of neighbor voxels as follows. If two neighboring cubic voxels are of the same phase (e.g. pore), the connectivity coefficient of the bond connecting them is equal to the micro property of these voxels (e.g. relatively put to be 1 for pore and 0 for solid). If two voxels share a face, and are of two different conducting phases (e.g. pore and hydration product), the connectivity coefficient of the bond connecting them is calculated from series connection of two conductors:

$$c_i = 1/(0.5 D_i^{-1} + 0.5 D_{i+k}^{-1})$$
(6)

where k = 1, w, or (w h) helps to represents shift of voxel numbering *i* to neighbor voxel in x, y, or z direction (Fig 3). The FD (second order) scheme is used to discretize the Laplace's equation. The Laplace's equation in finite difference form, at each node *i* (numbering shown in Fig 2) looks like this:

$$c_{x,i-1}u_{i-1} + c_{y,i-w}u_{i-w} + c_{z,i-wh}u_{i-wh} + + (c_{x,i} + c_{x,i-1} + c_{y,i} + c_{y,i-w} + c_{z,i} + c_{z,i-wh})u_i + + c_{x,i}u_{i+1} + c_{y,i}u_{i+w} + c_{z,i}u_{i+wh} = 0$$
(7)



Figure 3. Example of numbering of the voxel nodes for FD implementation, position and size of coordinates: width (x), height (y), and depth (z). Each shearing surfaces between neighboring voxels in x, y, and z directions have assigned connectivity coefficients c_x , c_y , and c_z , respectively.

Assembling all of these N equations together forms a system of global equations which can be represented in a matrix form:

$$\mathbf{A}\mathbf{u} = \mathbf{b} \tag{8}$$

where **u** is the voltage vector (size of the total number of voxels in the system, *N*), **A** is a sparse and symmetric matrix with 7 diagonals that contain information about connectivity coefficients of all the bonds among voxels, and **b** is the vector of knowns (i.e. boundary condition on top of the last layer: u(x,y,z = d + 1) = 1, Fig 1). The numerical model can be run using two types of side boundary conditions: 1) zero flux (adiabatic) boundary conditions, or 2) periodic boundary conditions. Equations (7 & 8) are adjusted in order to account for periodic boundary conditions (detailed later in chapter 3.3). The obtained system of equations (8) is solved by conjugate gradient algorithm (chapter 3.2).

Next, the flux in z direction at each node i, $J_{i,z}$ was obtained by solving the Fick's first law (eq. (5)). The FD scheme used is:

$$J_{i,z} = 0.5 \left((u_{i-wh} - u_i) c_{z,i-wh} + (u_i - u_{i+wh}) c_{z,i} \right)$$
(9)

The total (effective) steady state flux J_{eff} is calculated by averaging fluxes in the total system volume (total number of nodes N = w h d).

$$J_{eff,z} = \left(\sum_{i} J_{i,z}\right) / (whd)$$
(10)

Then D_{ef} was obtained easily from eq. (3). Lastly, the results of the numerical simulation are backed up with a high level of graphics visualisation to help investigating the results of transport simulations.

3.1 *Transport through capillary pores and hydration products*

The simulation of transport properties is implemented in two ways: 1) through capillary pores only; or 2) through capillary pores and hydration products (more precisely CSH gel). The diffusion process is dominated by the capillary pores as long as they are connected (i.e. percolate). In this case, the transport through the gel pores of CSH is neglected. Indeed, for porosities above the capillary pore percolation threshold (Koenders 2012), the transport is dominated by the capillary pore space because its transport coefficient is much higher (by a factor of 400) than the CSH gel. Nonhydrated cement grains and portlandite (CH) may be considered to be impermeable.

If capillary porosity is below critical percolation threshold, the transport is influenced by transport through capillary pores as well as CSH gel pores. This is because of the layered nature of this gel that has continuous gel pores. Only CSH can be considered as permeable, while CH as non-permeable. The Hymostruc 3D microstructure simulation does not distinguish CSH separately, but combines all hydration products in inner and outer hydration product. According to general effective medium theory (Zhang 2011), the effective transport coefficient of all hydration products (D_{hy}) can be estimated as:

$$D_{hp} = \left[1 + f_{CH} / ((1 - f_{CH}) / 3 - 1) \right] D_{CSH}$$
(11)

where *f* represents volume fraction of the corresponding hydration product.

3.2 Conjugate gradient solver with an optimized matrix-vector multiplication

Because the size of the sparse matrix A is N times N the matrix is not stored explicitly but only implicitly in the vectors \mathbf{c}_x , \mathbf{c}_y , and \mathbf{c}_z which store the conductance coefficients of the bonds among voxel faces in the x, y, and z directions, respectively. The system of equations (8) is solved by conjugate gradient algorithm. The bottleneck in this solver routine is the multiplication of matrix A with an arbitrary vector **a**. In order to speed up this solver one needs to do the multiplication in an optimized way. This is done by multiplying only the elements of the matrix that lie on the 7 diagonals and avoiding multiplications with very large number of zero elements. For solid voxel *i* the result of multiplication simply equals $\mathbf{a}(i)$. This 7 diagonal vectors contain conductance information and correspond to 7 terms in eq. (7). The elements on the central diagonal contain the coefficient obtained by summing all the 6 conductance coefficients that are connecting the central voxel to neighbors in x, y and z direction. Elements on other (non-central) 6 diagonals contain one corresponding conduct-ance coefficients.

3.3 *Periodic boundary conditions*

For calculating effective transport properties based on steady state model (4) employing p.b.c. is physically much more realistic than adiabatic (zero flux) boundary conditions on faces perpendicular to the imposed flux (Fig 1). Furthermore, p.b.c. implementation may enable the use of smaller representative elementary volumes and hence improve system resolution with negligible impact on computational cost.

The periodic boundaries were implemented differently than in Garboczi's FD code (Garboczi 1998). Here the p.b.c. were implemented without addition of extra shell layers around the system. There are 4 boundary faces that are parallel to the imposed flux across z direction: two (left and right) in y-z plane named yzL and yzR and two (up and down) in x-v plane named xvU and xvD. The voxels at the y-z left face (yzL) were connected with the corresponding (z-layer) voxels in the right face (yzR), and vice versa. Similarly, for x-y faces: voxels on upper face xyU were connected with the down face xyD, and vice versa. In that way the flux that goes out of the system from one face, enters into the system from the other face (e.g. *xyD*). For example on system in Fig 2, boundary voxels (xyU) 1, 2, 3, 4, 5, 6 and 7 are connected with boundary voxels (xyL)36, 37, 38, 39, 40, 41 and 42, respectively. Similarly in y-z plane, boundary voxels 1, 8, 15, 22, 29 and 36 are connected with boundary voxels 7, 14, 21, 28, 35 and 42. Voxels at the edges of the system have two opposite boundary neighbors (Fig 2) in y-z plane and in x-y plane. In previous example one can see that voxel 1 is connected with voxel 7 and with voxel 36. Two additional coefficient vectors (\mathbf{p}_x and \mathbf{p}_y) are used in implementation of p.b.c., each with the length of the number of the voxels in the one face of the system: e.g. length = $(h - 2)^*w$. These two vectors store the conductance coefficients for each boundary-boundary connection. If one of the voxels from each side is solid (zero conductivity) then the conductance coefficient linking the two sides is zero (no connectivity, and no flux). After the main matrix-vector multiplication according to eq. (7) the result was corrected on boundary nodes in order to account for periodic boundary conditions.

4 SIMULATION OF 3D MICROSTRUCTURE

Numerical model Hymostruc is applied that can be used to simulate the development of an evolving virtual microstructure of cementitious materials (van Breugel 1992). Hymostruc simulates the development of the 3D microstructure as a function of the particle size distribution, the water-cement ratio, the chemical composition and the temperature of the mix for cement hydration. The cubic size of simulated system is $100^3 \ \mu\text{m}^3$. The simulation is run on Portland cement CEM I 42.5 N (Blaine 420 m² kg⁻¹, $d_{\text{min}} = 1 \ \mu\text{m}$, $d_{\text{max}} = 50 \ \mu\text{m}$) with a water to cement mass ratio of w/c = 0.45 at 20°C.

The outer expansion of the particles is calculated according to the so-called particle expansion mechanism. A detailed description of the original Hymostruc model is given in (Breugel 1992). In this paper we consider only silicate reactions. The aluminate-bearing clinker minerals, i.e. C_3A and C_4AF , are not taken into account in the microstructural development. The next step in our research is to include the volume expansion of particles due to hydration reactions of non-silicate clinker minerals and pozzolanic materials (Koenders et al. 2012, Ukrainczyk et al. 2012).

First, the cement particles are put in a system to form an 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 according to the particle size distribution. During hydration, microstructure of material and amounts of certain phases are changing. Volume fractions of reactants, i.e. the non-reacted cement and the free water, decrease, while the total fraction of the formed hydration products increases, during the setting and hardening. The solid fraction comprises the fraction of non-reacted cement grains and the formed hydration products: inner, outer and contact hydration product. The simulated microstructure of hydrated cement paste is shown in Fig 1. Location of solid particles is described by following six parameters in 3D Cartesian coordinate system: the center coordinates of particles (x, y, z), the diameter of nonhydrated cement grain, and the layer thicknesses of inner and outer hydration product. The simulated microstructure is digitized (voxelized) into a 3D matrix of cubic voxels with a resolution of 1 µm/ voxel and 0.5 µm/voxel.

5 RESULTS AND DISCUSSION

5.1 Comparison between numerical and experimental results

Diffusion of tritiated water molecule (T_2O , hydrogen atom replaced with tritium) is simulated in order to investigate physical transport process



Figure 4. Visualizations of the distribution of water concentrations in cement paste at steady state: a) 3D slices of the capillary pore structure, b) Transport through capillary pores and hydration products, and c) 2D slices with cursor that actively changes the *z* position of microstructure.

Table 1. Comparison between simulated and experimental literature data.

| 90 days w/c = 0.45 | $\frac{D_{\rm ef} \rm sim.}{10^{-10} \rm m^2/s}$ Resolution | | $D_{\rm ef}$ meas., | Cap. Porosity, % | | |
|-----------------------|---|------------------|------------------------|------------------|-----------|------------------|
| Transport through | | | | | simulated | |
| | 100 ³ | 200 ³ | m^{2}/s | measured | 1003 | 200 ³ |
| capillary porosity | 1.12 | 1.13 | 0.1 | 22.2 | 22.5 | 18.9 |
| + hydrates | 1.37 | 1.17 | | | | |

independently of chemical interactions. At 20°C diffusion coefficient of water is $2.05 \ 10^{-9} \ m^2 s^{-1}$. The effective water diffusivity coefficient is investigated for hydrated cement paste and compared against the literature experimental data. The simulated microstructure of hydrated cement paste with visualization of the distribution of water concentrations (relative values 0–1) in cement paste at steady state is shown in Fig 4. The black parts show the high concentrations and the light grey (white) parts the low concentrations of species. Graphical 3D

and 2D output interface enables to interactively show 3D and 2D slices with a help of cursors that change the size of cube and z position of microstructure. This enables a full insight into the 3D numerical results.

The obtained numerical results are compared against an experimental data taken from literature (Delagrave et al. 1998). The experimental conditions were: cement ($C_3S = 68.7\%$, $C_2S = 6.9\%$, $C_3A = 7.7\%$ and $C_4AF = 5.4\%$) mixed with water to cement mass ratio of w/c = 0.45 and hydrated in saturated lime solution at 23°C for 90 days. The tritiated water diffusion test was carried out for about 4 months. Comparison between measured paste porosity and the simulated capillary porosity is shown in Table 1. The simulated capillary porosity is somewhat lower than the experimental. The simulated effective diffusion coefficient of tritiated water is higher than the literature value. This discrepancy could be due to a long time needed to obtain steady state conditions in real experiments. During such experimental conditions the continuing cement hydration evolves the microstructure, which is not considered in simulations. Hence, the simulated water diffusivity coefficient is indeed expected to be overestimated. The simulations were run with two resolutions: voxel length of 1 and 0.5 µm. Only a small difference in results can be observed while increasing resolution. Simulations run on Intel® Xeon® CPU3565 3.2 GHz, take 40 s and 9 min for resolution 1 m/voxel (100³ voxels) and 0.5 m/voxel (2003 voxels), respectively. The difference between simulations considering transport through capillary pores only and capillary pores together with hydration products is small due to high connectedness (percolation) of the system at investigated porosity (Koenders 2012).

6 CONCLUSIONS

This paper presents a full 3D finite difference module that has been implemented within original Hymostruc kernel with which the mass transport through an evolving microstructure can be evaluated.

The simulation of transport properties as described here can be viewed in a larger general aspect because of the analogy between the following four laws: Fourier's law for heat flow, Ohm's law for electric current, Fick's law for diffusion, and Darcy's law for liquid (and gas) flow in porous materials.

In future work hydration effects (e.g. impacts of portlandite distribution, aluminate-bearing hydration products and fillers) on transport properties will be investigated by linking virtual microstructure simulations and the developed 3D numerical transport model.

ACKNOWLEDGEMENT

This work was supported by the *Marie Curie* Actions EUgrant FP7-PEOPLE-2010-IEF-272653-DICEM, the postdoc personal grant from the National Foundation for Science, Higher Education and Technological Development of the Republic of Croatia, and Fred Schilperoort help with programming.

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