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DEMONSTRATION AND VALIDATION BY SIMPLE EXAMPLES OF A COMPLETE ANALOGUE POROSIMETRY METHODOLOGY FOR VIRTUAL CEMENT PASTES ON MICRO-LEVEL

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ABSTRACT

Details of a complete methodology for porosimetry of virtual concrete have been described in a series of publications. This paper shortly sketches the main characteristics, whereupon it is indicated how a pore network model is designed based on data extracted from the virtual cement paste. This involves smoothing the main trunks as the main pore connections between outer surfaces. Network estimates for water transport through concrete is presented and shown exceeding commonly used MIP estimates. For quantitative image analysis results the gap will be much smaller, though. Moreover, experimental data are biased by continued hydration (self-healing effects). Some simple examples are presented to improve the insight into the methodology. Moreover, they can additionally serve as validation by comparing estimates with analytical results.

Keywords

Cement, DEM packing, hydration, pore delineation, pore size and shape, pore network, permeability

INTRODUCTION

On the various "building blocks" for porosimetry, applicable to virtual cement pastes, we have been publishing earlier. It involves successively the packing of (so far) spherical cement particles by DEM [1,2], the hydration simulation by the improved vector approach, XIPKM [3], pore delineation including the assessment of the pore network topology by DRaMuTS - inspired by the path planning algorithm (RRT) of robotics [4] - and the assessment of pore geometry by star volume measurements (SVM) [4]. From the pore network structure, the main trunks are extracted and smoothed by a mathematical operation. Finally, a tube network system is designed on the basis of the geometrical and topological information obtained on this pore network structure. The tube system incorporates the throat size and shape variations along a tube element. Each tube element is subjected to a water pressure gradient. Fulfilment of the mass conservation law leads to a system a *n* algebraic equations for *n* nodal pressures in the network system. This is proven far more efficient than application of common FET.

More common in concrete technology are particle packing systems based on random sequential addition (RSA). RSA packing capabilities are limited, however major objection to its use for the present purpose is its biased dispersion of the particles [1,2,5]. This has inevitable effects on pore size distribution and on the pore depercolation process during hardening, and thus on pore network topology [2,6]. A survey of present-day's major RSA systems is available in [2]. The same publication also refers to other DEM systems used in

concrete technology and to the digitized approach developed at NIST, which also leads to biases in pore size distribution and pore depercolation during hardening [2,6]. In general, RSA will lead to too ordered, the digitized approach to too chaotic dispersion characteristics as compared to DEM. DraMuTS offers a more economical alternative for the serial sectioning and 3D reconstruction methodology developed by Ye for cementitious materials [7]. The random walk approach used elsewhere [8] has obvious similarity with the rapidly exploring random tree (RTT) algorithm of robotics [4]. An upgraded version constitutes the basis for DRaMuTS. SVM is a method developed and widely employed in life sciences for 3D estimation of the size of dispersed phase (such as pores) on the basis of 2D observations [4,8].

Estimates on water transport through the pore tube network derived from this microlevel vector-based virtual cement paste confirm outcomes of other vector-based approaches [9], but exceed MIP-based experimental data by about three orders of magnitude. It should be remarked, however, that the quantitative image analysis-based pore size distribution can be two orders of magnitude away from MIP data [10], so bridging a major part of the aforementioned gap. Moreover, experimental data are additionally reduced by self-healing effects during testing [11]. Nevertheless, we are working on application of nano-level CSH particle packing to model the last stage of the hydration process. This will lead to some reduction in pore size and connectivity, and to the development of rough-surfaced pores. All three factors will cause a reduction in transport capacity of the pore network system. Finally, experimental studies cannot guarantee full saturation of the specimens as assumed in the simulation; the dramatic consequences on permeability will be outlined on this conference in another paper.

With detailed publications available on the "building blocks" of the complete methodology, we will now concentrate on further data extraction for the construction of the tube network structure and on the presentation of simple examples that may provide insight into the complete methodological process and additionally serves as validation by comparison with analytical results.

RESUME OF METHODOLOGICAL CHARACTERISTICS

DraMuTS leads to the formation of trees, consisting of vertices and nodes, to penetrate from random seeds on the external specimen surfaces into the complicated and tortuous pore system. Improvements in the robotics algorithm to reduce computer efforts [12] cause violations in the uniform randomness of the dispersed points. Hence, a second "random" point system is superimposed. This renders possible analysing the topology of the network, allowing among other things the extraction of the main trunks as the principle connections between external surfaces. Neighbouring trees connecting different seeds may be joined on a large number of points. The extracted main trunk are the major pathways through the material. They are delineated by zig-zag lines. These should be smoothed to obtain proper values for pore tortuosity and trunk length. Fig. 1 illustrates in 2D the effect of mathematical smoothening on the pore network system. This requires a number of iterations as demonstrated in Fig. 2.

A network of tubes can be constructed on the basis of the main trunks. Nodes in the network system indicate connections between the main trunks. A random set of plane sections per randomly dispersed point inside pore space is investigated by SVM to find the minimum or so called throat section. The equivalent tube diameters of the throat sections govern the size along the tubes. A shape factor is finally introduced by $Sh = A/P^2$, with A and P as the area and perimeter length of the throat section. This will to foresee in the differences in conductance of the pore throat section (Fig. 3) and its equivalent circular section [11].

Demonstration and validation by simple examples of a complete analogue porosimetry...

To obtain the conductance of all equivalent tubes, the cross-section's hydraulic conductance can be calculated at the pore throats along the main trunks. However, solving the flow by FEM at every pore throat would be not practical. Therefore, the influence of the shape factor on conductance is integrated statistically. The conductance is estimated by FEM at an adequate number of random points in pore space. The obtained values are then used to form a linear function to obtain the conductance for any pore throat via its shape factor. This graph is shown and fitted by a linear function as in Fig. 4. It should be noted that the shape factor for a circle is $Sh=1/4\pi$ and its conductance $C = (\pi D^4/128\mu)$, the latter under the conditions of no slip at the wall and a parabolic flow distribution.

The volumetric flow rate, Q_{ij} , in a tube segment with a pressure difference between the two ends (*i* and *j*) can be expressed by

$$Q_{ij} = G_{ij}(p_i - p_j)$$

(1)

where G_{ij} denotes the hydraulic conductance of the tube segment and p_i and p_j are the applied pressures at the two ends of the segment. At each node *i* that connects a number of the tube segments, the mass conservation law of flow gives

$$\sum_{j=1}^{n_i} Q_{ij} = 0.$$

(2)

where n_i is the total number of tubes having node *i* as the common end, and *j* denotes the other ends of the tube.



Fig. 1. Illustration of main trunk smoothing (left) and results illustrated in 2D pattern (right)



Fig. 2. Decrease in total length of main trunks by mid-point (MP), end-point (EP) and combined (Comb) smoothing operations (10 times MP followed by 10 times EP).



Fig. 3. Velocity field (in relative terms) solved by FEM of flow through an irregularly-shaped pore throat section.



Fig. 4. Conductance C of pore throats as a function of the shape factor *Sh*, both in relative terms (note that indices po and cir refer to pore and circle, respectively)

Substituting Eq. (1) into Eq. (2) yields a set of algebraic linear equations with nodal pressures as unknowns. Applying the prescribed pressures at the nodes (tube ends) located at

the bottom and top surfaces of the specimen, the nodal pressures are determined by solving the linear system of equations. The flow rate in each tube and thus the total outlet (inlet) flow rate can be calculated, whereby the average velocity of flow and therefore permeability can be determined. So, *size and shape* are included in this solution

SIMPLE EXAMPLES AS ILLUSTRATION AND VALIDATION

Two solid cubes with side length of 100 units contain hollow square-sectional tubes going through the specimens from bottom to top surfaces. The solid phase is constituted by densely overlapping spherical particles with a radius of 2.5 units placed at spacing of 2.5 units in all dimensions. The tubes inside the specimens are created by removing a number of spherical particles. The configuration of the tubes in the two specimens is schematized in Fig. 5. Case I contains tubes with different sizes, whereby the throat size distribution of pores estimated by DRaMuTS can be validated. Case II contains different types of tubes expressing the isolated pores and the main-path versus branching dead end pores of the percolated pore system [11].



Fig. 5. Configuration of tubes in the specimens

The walls of hollow tubes are not perfectly flat but shaped by the surfaces of the spherical cement particles, leading to differences in throat size between SVM and actual assessment. The intrinsic permeability values of the specimens obtained by DRaMuTS are compared to those by analytical calculations, presented in Table 1. The difference in permeability values is again caused by the imperfect tube walls; the analytical values are estimated on the basis of ideally square tubes (with side length a) of which the conductance is given by

$$C_{square} = \frac{7a^4}{200\mu} \tag{3}$$



Fig. 6. Expansion of trees in the two cases of Fig. 5



Fig. 7. Extracted main trunks before (top) and after (bottom) smoothing



Fig. 8. Throat size distribution of Case I.

Table 1. Intrinsic permeability (squared length units)

Specimen	Case I	Case II
DRaMuTS	0.278	2.837e-3
Analytical	0.228	3.153e-3

VIRTUAL CEMENT SPECIMENS AND VALIDATION

Cubes with 100 μ m rib length were produced of virtual cement pastes of which two types are shown in Fig. 9, whereby W25 stands for a water to cement ratio of 0.25. F300 denotes a Blaine fineness of 300 m²/kg. *p* indicates global porosity. Hydration duration is shown in the caption. The DRaMuTS-produced pore trees are also depicted in Fig. 9, while the main trunks are shown in Fig. 10. Next, these main trunks are mathematically smoothened and geometric properties are used for the estimation of permeability by way of the tube network structure, which yielded the values presented in Table 2. Values of bulk zone, ITZ and composite specimen are separately listed. These permeability values of the simulated cement pastes predicted by the proposed methodology agree well with other vector-based simulations of cement paste with spherical particles. As an example, Pignat *et al.* [9] report an intrinsic permeability of a simulated cement paste (w/c = 0.4) with a total porosity of 19% and K=3.4e-15 (m²). Hence, this validates the methodology for a more complicated, realistic case.

Table 2. Intrinsic permeability (m^2)

Code	W25F300	W40F420
Coupled ITZ+bulk	1.446e-16	1.600e-15
Bulk	7.522e-17	1.270e-15
ITZ	3.643e-16	3.102e-15



W25F300 (90 days, p = 9%)

W40F420 (60 days, p = 19%)

Fig. 9. Exploration by 60,000 virtual vertices for each matured cement specimen



Fig. 10. Extraction of main trunks from virtual trees in matured cement specimens

DISCUSSION

Nonetheless, the permeability estimated on simulated cement pastes are higher than experimentally measured. This is discussed in the introduction of this paper. The vector-based set up for analogue representation has its shortcomings, however also experimental set ups are not well-defined (self-healing, degree of water saturation, *etc*). As investigated by Muller *et al* [13], the smooth surface of the hydration deposits is an obvious deficit, since surface roughness can significantly reduce conductance of a pore throat section. Such a surface roughness could be simulated by having the top of the outer layer of CSH simulated as a nano-particles-packed structure (Fig. 11). This will lead to some pore size reduction. Moreover, this will give rise to so called "bottle necks" in the vector-based pore network structure to (partly) close off. Hence, the pore continuity could be disproportionately reduced. When combined, these effects will at least bridge part of the gap between experiments and simulations. Finally, the estimates are based on *fully saturated pores*, a situation that cannot simply be realized in tests. These aspects are discussed in a separate paper [14,15].



Fig. 11. Fibrous C-S-H consisting of nano-particles (blue circles) grows from the surface of cement grains (red circles) in 2D space. (left) early age of hydration process; (right) late age of hydration process. Periodic boundaries are employed in this case.

CONCLUSIONS

The complete methodological set up is based on the vector approach, so is an *analogue* simulation method. Particle packing of the cement grains is by DEM, which leads to superior results as compared to the in concrete technology more popular RSA approach. Superiority holds for reliability, economy as well as versatility (*e.g.* higher cement contents at very low water to cement ratios). The robotics-inspired pore delineation system, DraMuTS, compares favourably in economy with the serial sectioning and 3D reconstruction approach by Ye [7]. It has some similarity with random walk approaches used for this purpose in *voxelized* virtual hardened cement paste systems. The tube network representation for the pores in hardened cement paste is for vector-based approaches shown more economic than doing this by FET.

The estimates on permeability are of the same order of magnitude as published data also obtained by the vector approach, yet data are significantly higher than experimental observations based on the most popular MIP method. More realistic values obtained by quantitative image analysis will thus be much closer to the simulation estimates. The small gap that nevertheless will be left is due to the inherent deficits of the experiments based on water transport through concrete (due to self-healing effects) and of the vector approach, yielding layers of uniform thickness with a smooth surface on an hydrating cement particle. Nano-level packing by DEM of particles in the outer layer of the hydration deposits can lead to improvement as a result of some pore size reduction, formation of rough surfaces and increased pore depercolation.

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