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DOI

[10.1680/jmacr.16.00356](https://doi.org/10.1680/jmacr.16.00356)

Publication date

2017

Document Version

Final published version

Published in

Magazine of Concrete Research

Citation (APA)

Stroeven, P., & Li, K. (2017). A modern approach to porosimetry of virtual cementitious materials. *Magazine of Concrete Research*, 69(23), 1212-1217. <https://doi.org/10.1680/jmacr.16.00356>

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A modern approach to porosimetry of virtual cementitious materials

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To assess the pore size of virtual cementitious materials, the star volume method (SVM) can be considered an effective tool. Unfortunately, the SVM requires a large number of plane sections in each of the very large number of random points, resulting in a time-consuming and expensive operation. As a more economical alternative, this paper presents a stereology-based contracted method, which uses a well-known theoretical concept proposed by Cauchy. This method completed pore size measurements in a shorter period of time (reductions as high as 85%) while demonstrating reliability to be maintained at the same level.

Notation

A_i	random section area
A'	throat area of a pore
$d_{0.5}$	median two-dimensional pore throat size
$d_{0.5\text{rand}}$	median two-dimensional (2D) pore size based on random sections
$T_{\min\text{SD}}$	2D minimum (throat) size distribution
T_{ranSD}	random section size distribution
θ	orientation of random section

Introduction

Fluid transport through the pore network structure that develops during the hardening of cementitious materials can cause premature degradation of the material, and extensive research studies focusing on various aspects of this matter have been conducted. However, the reliable estimation of permeability levels for engineering applications of concrete structures is not an easy task, and time-consuming experiments such as by mercury intrusion porosimetry (MIP) and image analysis techniques are generally necessary. The alternative of using virtual reality approaches should thus be given serious consideration. A reliable and quite economical methodology has been developed for that purpose by the present authors, and all the details are available in the literature (Li *et al.*, 2015; Stroeve *et al.*, 2015). These works also deal with alternative approaches employed in concrete technology and validation of the method using experimental and other numerical studies. More extensive references to other approaches are also available (Mechtcherine *et al.*, 2014; O'Connor, 1996; Stroeve *et al.*, 2009). The virtual standard approach developed by the current authors allows solutions to be found in terms of hours instead of the weeks or months required for more systematic experimental research work.

Virtual approaches start with a material's microstructure obtained upon simulating the hydrated cementitious binder.

This is accomplished through packing of the binder particles using the discrete-element method (DEM) instead of random sequential addition (RSA) algorithms, which are (almost exclusively) popular in concrete technology (Stroeve, 1999; Stroeve *et al.*, 2009; Williams and Philipse, 2003). This step is followed by application of the vector-based extended integrated particle kinetics model (XIPKM) (Le *et al.*, 2013). In doing so, a virtual microstructure is made available for porosimetry analysis. The tortuous and complex pore space is the result of the reducing space left by hydrating particles and the pore de-percolation process during hardening. Hence, the continuity in major transport channels, relevant for permeability estimation, gradually diminishes.

The exploration and quantitative assessment of the geometric properties of the main transport channels is the goal of porosimetry. Double random multiple tree structuring (DRaMuTS) and the star volume method (SVM) can be used for this purpose. DRaMuTS is an approach inspired by the rapidly exploring random tree method developed in robotics by LaValle and Kuffner (2001). Trees, consisting of nodes, and connecting straight line segments grow in the pore space and are forced to merge when they are in the same pore section. Hence, in this way, pore topology, whereby the main channels are separated from the rest of the pore space (isolated pores and pores branching off the main channels), can be assessed. The pore-measuring module SVM was originally developed in spatial statistics and is now widely used in life science experimental setups. In this method, a random plane pore section is selected from all nodal points inside the pore space, and its size (i.e. of the representative circle) is obtained by means of two-dimensional (2D) stars. By considering an isotropic uniformly random (IUR) set of such plane sections in all points, the one with the smallest area is assessed. This is called the local pore throat. All throat sizes are used for the construction of a 2D pore size distribution function. The zig-zag tree branches inside the pores are smoothed by a mathematical operation,

which makes assessing the pore lengths between the nodes possible. The data obtained on the geometric properties of the pores (such as size, length and shape) are necessary input parameters for setting up a pore network model for predicting permeability. The tube model for permeability estimation has been explicitly described elsewhere (Koster *et al.*, 2006; Le, 2015; Li *et al.*, 2016; Pignat *et al.*, 2005).

This paper concentrates exclusively on an elegant way of shortening the stage for quantitative assessment of the geometric properties of the main transport channels. The standard SVM, which has been analytically validated by Le (2015) and Li *et al.* (2015), is used as a reference method. In general, 10^5 nodal points are required in a $100\ \mu\text{m}$ cubic container to ensure reliable results. An expensive calculation can be expected if the SVM is applied to all 10^5 nodal points, since many sections are necessary for each point. To reduce computational effort, this paper presents a method that uses Cauchy's concept for the average total projected area of surface area in space (Cauchy, 1882; Stroeven and Hu, 2006); this implies that a single 'randomly' selected section instead of a large number per node is required to obtain reliable geometric information. The resulting reduction in computational effort can be as high as 85%, while reliability is maintained at the same level. This method can thus be considered a breakthrough in economising porosimetry using the validated standard method. The standard method is outlined in the next section and then used as a reference for the new contracted approach.

Porosimetry methods

The standard approach (reference method)

This modelling approach starts by designing the particulate material; that is, selecting a particle range and an appropriate particle size distribution, for which the so-called Rosin–Rammler distribution is commonly used. This is given by

$$1. \quad G(d) = 1 - \exp(-bd^a)$$

in which $G(d)$ indicates the mass or volume fraction of spherical cement grains passing a sieve with opening d , and a and b are constants.

This particle ensemble is then dispersed by an RSA algorithm in a relatively large container and thereupon set to linearly move and collide according to Newtonian laws in a force-based dynamic DEM system. At the same time, the container is reduced in size. When the particle density (and thus the water to cement ratio (w/c)) is in agreement with the paste's design, the dynamic stage is terminated. The start and end situations are illustrated in Figure 1.

The packed binder particles are then hydrated using the simulation system XIPKM (Le, 2015). This is a vector (geometry-based) approach, so that the pore microstructure will be

Figure 1. Process of packing simulation in the DEM: (a) dilute dispersed spherical binder particles in a cubic container with periodic boundaries before packing; (b) mixture after dynamic packing to the desired density followed by some size compensation (enlargement) for visualisation purposes

formed by a succession of spherical elements resulting from interferences of hydrating particles (Bishnoi and Scrivener, 2009; Jennings and Johnson, 1986; Navi and Pignat, 1999). As examples, sections of hydrated plain cement and rice husk ash blended cement paste cubes are presented in Figure 2. Calcium silicate hydrate (CSH) and calcium hydroxide are the main hydration products in the paste (Shen *et al.*, 2016). A 3D view of the resulting nature of the simulated pore structure is given in Figure 3, in which all the solid phases have been removed. XIPKM has been extended to cover all major cement compounds (Le *et al.*, 2013). However, since this aspect does not interfere with the realisation of the target of this paper, this complication is eliminated for the present purpose.

The next stage in the procedure is to explore this pore phase using DRaMuTS. For this purpose, 10^5 nodal points are uniformly and randomly dispersed in the pore space, whereupon tree structures are generated, starting from seeds at the specimen surfaces, connecting nodal points by straight lines. When a connected line is intersecting with the pore surface, the nodal point is shifted along the straight line to avoid an intersection, as shown in Figure 4. This number (10^5) of nodal points is selected because any increase does not significantly influence the outcomes (details of the sensitivity analysis are presented by Stroeven *et al.* (2012)). The SVM is then applied to assess the pore size in each local point, such that the pore size distribution function can be obtained and used for comparison purposes, or – in a next step – for permeability estimation. Alternatively, and more relevant for permeability estimation, the size of the smallest 2D sections (so-called throats) in the pore system at the location of dispersed points are determined. For that purpose, the SVM has to be applied in 2D to a series of IUR distributed pore sections in all 10^5 points, whereby the pore size is associated with the size of the local representative circle. For illustrative purposes, the two types of pore size distribution functions are shown in Figure 5 for a similar case.

Figure 2. Sections of cubes with periodic boundaries: (a) plain cement paste, $w/c = 0.4$; (b) cement paste blended with 20% rice husk ash, $w/c = 0.4$. The pore structure (in black) is of a tortuous and complex nature

Figure 3. Three-dimensional visualisation of pore space ($w/c = 0.26$; 10 years of hydration) (Stroeven, 1999)

Figure 5. Volume-based 3D pore size distribution function and 2D throat size distribution function obtained by SVM (specimen W40F300 (i.e. $w/c = 0.4$; Blaine fineness = $300 \text{ m}^2/\text{kg}$))

Figure 4. Rapidly exploring random tree procedure in robotics would lead to rejection of point 1 because of intersections (3) with particle surfaces. Instead, in DRaMuTS, point 2 is neglected and a new point (point 4) is generated to avoid such intersections

The contracted approach described in the next section is focused on reducing the effort required for this time-consuming task. In the following, the throat size distribution function in the standard approach is denoted $T_{\min}SD$.

Figure 6 shows that good agreement is obtained between the pore size distributions obtained by experimental image analysis and by the simulation methodology (Le, 2015). In contrast to MIP, image analysis seems to be more suitable for comparison purposes because MIP has been shown to produce too small pores because of the so-called ink-bottle effect, and accessibility of the mercury at specimen surfaces is limited (Diamond, 2000; Willis *et al.*, 1998).

The contracted approach: a new (Cauchy) concept

In this approach, no modifications in the DEM-based packing of the binder particles are made. Similarly, the vector-based hydration simulation approach is not changed. Both constitute appropriate modules or stages of a reliable porosimetry methodology. In addition, DRaMuTS offers a rigorous and efficient method for delineating a pore network system. The second

Figure 6. Pore size distribution of specimens with $w/c=0.4$ obtained by experimental image analysis techniques and by simulation (Le, 2015)

random point system was exploited for throat area assessment by the SVM. This method is more straightforward than the serial sectioning and 3D reconstruction technique proposed by Ye (2003). Of course, mathematical morphology techniques could have been applied as alternatives for obtaining the skeleton structure of the pore space (Serra, 1982). Nevertheless, pore sizes still have to be determined as major parameters underlying permeability estimations.

Since determination of the throat area per point is a quite time-consuming operation, a contracted approach was developed to optimise the procedure. Instead of assessing the throat area by numerically elaborating an IUR pore section system in all random points, only a single ‘randomly’ oriented section is employed in all points, and the respective areas are used for constructing an area-based section size distribution function, T_{ranSD} .

To derive a stereological relationship between the median pore sizes as depicted by the throat size distribution function (T_{minSD}) and the random section size distribution function (T_{ranSD}), the throat area can be imagined as being replaced by its representative circle, the size of which is determined by the SVM. So, a short element of the pore can be modelled as a cylinder of the same diameter. As a consequence, the randomly selected section can be envisaged as an ellipse through the centre of the representative circle, and the ellipse can be assumed to have the same area as the random section. Due to the large number of generated points, it is possible to collect, in an imaginary way, all local circular throats of equal diameter in order to yield reliable geometric information. The associated random sections will constitute an IUR set around the centre of the representative circle.

When a single elliptic random section of area A_i is projected onto the representative circle area over an angle θ_i , its projected area A' equals the area of the throat, $A' = A_{\text{min}}$. This is shown in Figure 7(b). So, for an IUR set of elliptic sections that are all projected on the same representative circle

Figure 7. Model for a local throat on the basis of its representative circle (b) and associated unit sphere (a) onto which infinitely small elements of the random section areas are collected. Projection of dA_i yields a $\cos$ term, whereas relative frequency is governed by a sine term (dashed line in (a))

area A'

$$2. \quad A' = \bar{A}_i \frac{\int_0^{\pi/2} \cos \theta \sin \theta \, d\theta}{\int_0^{\pi/2} \sin \theta \, d\theta} = \frac{1}{2} \bar{A}_i$$

where $\cos \theta$ represents the projection operation and $\sin \theta$ is the relative area of the unit sphere shown by the dashed line in Figure 7(a). This is also the relative frequency of infinitely small elements of sections $A_i(\theta)$ for $\theta = \text{constant}$. $\bar{A}_i$ is the mean value of A_i over $0 \leq \theta \leq \pi/2$ and A' is the throat area of all representative circles of equal size. Equation 2 is similar to Cauchy's solution for the average projected area of a surface element in space (Cauchy, 1882), although this surface has zero curvature in the case treated here.

The average projected area of the random set of elliptic sections of cylinder elements of similar diameter is thus twice the area of the throat in the same point. This holds for all subsets

of cylinder diameters of different size classes and thus for the actual collection of throats. As a consequence, T_{ranSD} has the same shape as in the standard approach, but is shifted by a factor of two towards larger areas. Since, instead of the area, the diameter of the representative circle is commonly used for T_{ranSD} , the shift will be $2^{1/2}$.

Validation results

Figure 8 shows the ratio of the median values of the size distribution functions of the standard approach (T_{minSD}) to the contracted approach (T_{ranSD}), $d_{0.5,\text{rand}}/d_{0.5}$. This ratio turns out to be very close to the theoretical estimate $2^{1/2}$, thereby validating the modelling approach. Figure 8 deals with 19 standard porosimetry results of different cementitious mixtures encompassing various values of w/c ratio and cement fineness, some of which were blended with a pozzolanic admixture. All the mixtures were also assessed using the proposed contracted approach. Additionally, the T_{ranSD} and T_{minSD} functions were of similar shape, as indicated in Figure 9 for some of the mixtures assessed in Figure 8. The random pore section distribution when horizontally ‘squeezed’ by a factor of $2^{1/2}$,

Figure 8. Size ratio of median values of random section and throat areas ($\approx 2^{1/2}$) for 19 different cases obtained, respectively, by the contracted method and the standard approach (Le, 2015)

maintaining the same unit area under the curve, can be imagined to lead to similar maximum values. However, this similarity between T_{minSD} and the size-corrected T_{ranSD} is not demonstrated in this paper, since the image would be too complicated if all the curves were presented on one figure.

The production of a cementitious pore microstructure involves three successive stages (DEM particle packing, XIPKM hydration simulation and DRaMuTS pore delineation) that require about 1 h computational time per stage – these times are similar in the full and contracted approaches. The pore-measuring stage (SVM) in the full approach also requires about 1 h of computational effort, but this is reduced to an average of 9 min in the contracted approach – that is 85% shorter than the full approach. This convincingly demonstrates the economy of the contracted approach, while Figure 8 proves the approach has the same reliability as the standard approach.

Discussion

The contracted approach of pore measuring requires six to eight times less computer time and thus computational time can be shortened by 85%. However, the method has a serious drawback, since the random section size distribution function (T_{ranSD}) is not linked to positions in the pore network. Hence, these data cannot serve as input parameters for the tube network model underlying permeability estimates.

Nevertheless, the simplified SVM approach for the assessment of pore throat size distribution is not only highly economical but is also reliable. It can be elegantly linked with (a limiting case of) the Cauchy concept for surface area determination on the basis of the average area of IUR projections in space. In the proposed method, the surface in space (i.e. the throat area) has zero curvature and the IUR set of projected areas is formed by the associated ‘random sections’. Finally, it should be noted that the throat area as well as the associated

Figure 9. Area-based pore size distributions of plain and blended specimens with different w/c ratios at 90 d of hydration, based on random section areas (contracted approach) (a) and (minimum) throat area (standard approach) (b). The value after W represents the w/c ratio (e.g. W25 means w/c = 0.25), F300 means a Blaine fineness of 300 m²/kg and R20 indicates a specimen blended with 20% rice husk ash (Le, 2015)

representative circle contain a random point. The described model is, however, based on the centre of the representative circle. An elliptic random section generated at such a random point can be shifted to the circle's centre, while maintaining its orientation in space, without modifying its size.

Although outside the scope of this paper, it should be noted that seemingly too large pores are obtained in numerical approaches such as those presented here. Three factors play a role in this. Firstly, it is recognised that MIP data that are generally used for verification purposes are biased with respect to more realistic quantitative image analysis results by, say, two orders of magnitude (too small) (Diamond, 2000; Willis *et al.*, 1998). Secondly, concrete (in practical cases microcracked) is generally used in experiments (Zhang *et al.*, 2017) whereas the numerical approaches consider cement paste. Finally, uncertainty in the water saturation degree in experimental setups that are generally based on supposedly fully saturated specimens leads to pore sizes being reduced to an unknown degree. A detailed discussion on this subject is given by Li *et al.* (2016).

Conclusions

A standard porosimetry method and a newly developed contracted approach were applied to a wide range of cement-based materials. The ratios of median pore throat sizes were found to be in good agreement with the Cauchy concept ($2^{1/2}$), which presents an estimate of the surface area in space by averaging the total projected area on randomly oriented planes. The contracted method applies this to the planar throat area, and so is a limiting case. This agreement can be viewed as validation of the contracted approach presented in this paper, which offers optimised porosimetry conditions for DEM-simulated cementitious materials.

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