# Size Characterization of Pore Structure for Estimating Transport Properties of Cement Paste

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## Summary

The conventional experimental approach to assessing pore structure characteristics in cement paste cannot provide reliable results. This problem can be approached by statistical and mathematical methods, *e.g.* stereological analysis and mathematical morphological measurements. The size characterization of pore space allows direct prediction of paste permeability with empirical relationships. Potential application for estimating other transport properties is briefly discussed based on pore network model.

## Introduction

Porosity and pore structure are of paramount importance with respect to the mechanical and durability properties of cementitious materials. The micro-structural development of cementitious materials and the relationship between structure and material property has been extensively studied by experimental techniques (*e.g.* mercury intrusion porosimetry) and in computer modelling approaches. However, accurate quantitative characterization of pore structure remains a challenge due to the complex and interconnected nature of the pore network in cement pastes and concretes. The reliability of most experimental techniques is limited since the interpretation of experimental data is based on assumptions of pore geometry that are largely deviating from those in reality. Moreover, numerical modelling of cement paste and concrete, when starting from non-realistic simulation of particle packing structure, cannot yield correct simulation results.

Size characterization during hydration of pore structure can be approached by quantitative image analysis techniques, stereological estimation, and by application of mathematical morphology methods. Stereological theory allows deriving three-dimensional (3D) structural information including volume fraction of porosity and specific surface area from specimen sections, thus dramatically reducing labour intensity of serial sectioning. At the same time, mathematical morphology measurements can be applied to section images of cement pastes for proper determination of pore size distribution. This paper deals with the application of these statistical and mathematical methods to size characterization of pore structure, and with its potential for estimating transport properties of cement paste.

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## Stereological analysis

Stereology encompasses geometrical statistical tools providing means for unbiased estimation of 3D geometrical parameters of the state of aggregation in materials on the basis of one-dimensional (1D) or two-dimensional (2D) observations [1]. Analogue as well as binary images (with pore space as phase of interest) of specimen sections can be subjected to quantitative analysis. Stereological theory allows straightforward measurement of volume fraction of pore space, *i.e.* porosity (●) from section images. Due to the finite resolution of images, the apparent porosity is slightly smaller than the total porosity because pores smaller than the resolution limit cannot be detected.

The perimeter length of 2D pore features per unit test area ($L_A$ in ● $m^{-1}$) can be assigned 3D stereological character via the relationship $s = 4\bar{L}_A/\pi$ [1], where *s* is the surface area of pore space per unit test volume (expressed in ● $m^{-1}$). Solid phase is complementary to pore space in section images of cement pastes. Therefore, stereological measurements of average size and spacing of solid phase provide information on pore spacing and pore size, respectively. Mean free spacing between solid phase clusters (● in ● m) reflects the spatial dispersion of solid phase, and can be adopted therefore as a direct representation of average pore size. Similarly, mean intercept length of solid phase clusters ($\bar{L}_3$ in ● m) indicates the average pore spacing. According to stereological theory, mean free spacing is associated with the volume and surface area of pore space, resulting in $\lambda = 4\phi/s$. Hence, $\bar{L}_3$ can be expressed in porosity and specific surface area by $\bar{L}_3 = 4(1-\phi)/s$.

## Mathematical morphology measurements

Two-point correlation function (TPCF) is a basic measurement in mathematical morphology. Let *Z*(*x*, *y*) represent a binary image with *Z*(*x*, *y*)=1 for pixels belonging to pore space, and *Z*(*x*, *y*)=0 for pixels belonging to solid phase, with the integers *x* and *y* representing the horizontal and vertical coordinates of a pixel. The apparent porosity is calculated as the average of *Z*(*x*, *y*). TPCF accounts for spatial structure in the images by considering each possible pixel pair

$$R_z(u,v) = \overline{Z(x,y)Z(x+u,y+v)} \tag{1}$$

where *u* and *v* are the lag distances in the *x* or *y* direction. The special case of zero lag distance, *i.e.*, $R_z(u=0, v=0)$ yields ● since $Z(x,y)^2 = Z(x,y)$ for binary pixels. With increasing distances the correlation function decreases to $R_z(u,v) = \phi^2$ for completely uncorrelated pixels. The correlation function can be calculated similarly for the solid phase. For presumably isotropic structures like ordinary cement paste, the matrix

$R_z(u,v)$ can be transformed into a 1D vector $R_z(r)$. The distance $r$ is relative to $u$=0 and $v$=0, where $u = r\cos\gamma$ and $v = r\sin\gamma$, with $\gamma$ representing the angle with the $x$-axis.

Specific surface area $s$ can be derived from the slope of $R_z(r)$ by taking the limit [2]

$$\lim_{r\to 0}\frac{dR_z(r)}{dr} = -s/4 \tag{2}$$

Dullien [3] proposed the concept of hydraulic radius of void space ($R_{hv}$), defined as the pore volume divided by wetted area. In the case of full saturation, $R_{hv}$ can be defined as the ratio of porosity and specific surface area ($\phi/s$). Since the surface areas of solid phase and pore space are the same, the hydraulic radius of solid phase $R_{hs}$ should be $(1-\phi)/s$. Hence, the stereological parameters characterizing pore size and spacing are associated with the hydraulic radii of pore space and solid phase by a constant factor of 4.

The measurement results of porosity and specific surface area, thus the hydraulic radius, depend on image magnification. Ultimately, $\phi$ is bounded by total porosity, but $s$ will increase dramatically at increasing magnification, resulting in smaller values of $R_{hv}$. Berryman and Blair [4] proposed a maximum magnification necessary for determining hydraulically relevant values for $s$ from section images.

Another important mathematical morphology measurement for size characterization is the so-called opening distribution [2, 5]. It is a size classification of pore space based on series of morphological opening operations by structuring elements of increasing size. The traditional approach of size characterization of individual pore features does not make much sense in view of the complex pore network of high tortuosity and connectivity.

## Application to section images of cement paste

The authors applied afore-mentioned stereological and mathematical morphology approaches to section images of cement paste specimens with different water to cement (w/c) ratios and degrees of maturity. In contrast to the conventional method yielding area histograms, the opening distribution technique provided appropriate characterization of pore size distribution in good agreement with experimental results obtained by Wood's metal intrusion porosimetry [5]. The morphological evolution during hydration of pore space can be analysed on the basis of the mean free spacing (*i.e.* average pore size). The depercolation threshold of capillary porosity, which is closely related to transport phenomena in cement-based materials, can be associated with a value of porosity whereby mean free spacing arrives at a stable value. The results obtained by this morphological approach are consistent with simulation results of Bentz *et al.* as well as with experimental findings of Powers [6].

TPCF is also instrumental for obtaining statistics of material microstructure, and has been used to estimate fluid permeability of sandstones [4] and soils [7]. It should be noted, however, that the size characterization approach by Berryman and Blair [4] contains some imperfections. They proposed a characteristic pore size $R_c$, defined as the intersection of the tangent of the correlation function at lag 0 and the horizontal line given by ●$^2$: $R_c = 4(\phi - \phi^2)/s = 4R_{hv}(1-\phi) = 4R_{hs}\phi$. It follows that $R_c$ is identical for the void space and the solid phase, and is strongly related to the hydraulic radius. This so-called characteristic pore size is equivalent to $\lambda(1-\phi)$, *i.e.*, $\pi\phi(1-\phi)/L_A$. It is *not* a characterization of pore size, but a length scale proportional to the linear dimension of the representative volume/area element (RVE/RAE). The RVE is the statistically homogeneous sub-volume of the material representative for bulk. The calculated $R_c$ is 2.4, 2.6 and 3.1 ● m, respectively, for cement pastes (w/c=0.5) at increasing hydration time (3, 7 and 14 days). This is corresponding to the increasing size of the RAE for more matured cement pastes [8]. Hence, it is obviously not a size characterization of pore structure since average pore size is *decreasing* during hydration process. Pore size can be assessed properly by the mean free spacing or by the correctly defined hydraulic radius.

Another important size characterization is based on the so-called critical pore size. This is defined as the size of the pore that completes the first interconnected pore pathway in a network developed by a procedure of sequentially adding pores of diminishing sizes to this network. This parameter is associated with the depercolation threshold of porosity. It can be determined from the inflection point of the pore size distribution curve. Supposedly, this is a monotonously decreasing function of hydration time for given cement paste.

Average pore size and pore spacing are involved in the phenomenon that measurement results (*e.g.* local porosity distribution and correlation function) are strongly dependent on size of measurement tools (*e.g.* measurement cell in local porosity analysis and lag in TPCF). Biswal *et al*. [9] employed the local porosity theory proposed by Hilfer *et al*. [10] to analyze local porosity distribution (● ) in different sandstone samples. They defined a characteristic length scale as the minimum linear dimension of measurement cell ($L$*) when the ● curve vanishes at both ends of porosity-axis (porosity equal to 0 and 1, respectively). They compared the ● curves of different sandstones at their respective values of $L$* and associated the width of the curves with heterogeneity of sandstones. This approach is also incorrect because $L$* defined in [9] is equal to average pore spacing. When the measurement cell is large enough to cover at least two pore features, the ● curve will present zero values at both ends of the porosity-axis. Hence, $L$* has no direct correlation with the length scale of the RAE. Characteristic length scale should be assessed in a different way [8]. The long-range fluctuation behaviour of correlation functions observed in a study of Schaap and Lebron [7] for soil structure can also be associated with size characterizations.

## Potential for estimating transport properties

The size characterization allows estimating permeability of cement pastes on the basis of Kozeny-Carman relationship. This empirical equation requires structural information encompassing porosity, pore size (hydraulic radius) and pore geometry. Schaap and Lebron [7] generalized the Kozeny-Carman equation by lumping the effects of all unknown factors (tortuosity and pore connectivity) into one single parameter $C$, leading to $k=\phi R_{hv}^2/C$. Their research on different soil samples revealed $C$ to be stronger correlated to permeability $k$ than porosity and hydraulic radius. This is consistent with the present authors' analysis of correlation between cement paste permeability and parameters characterizing pore structure [11]. Vogel [12] also stated that the way pores are interconnected may be even more important than pore size and connected fraction of porosity. Hence, it is necessary to incorporate structural information on pore topology in an approach pursuing accurately predicting paste permeability.

In the context of mathematical morphology, the connectivity function can be derived from measurements of the Euler characteristic as a function of pore size [12]. Another approach to topology quantification is provided by the concept of percolation probability. This denotes the probability to find a continuous path through a sample of given size. Percolation probabilities can be evaluated as a function of sample size and porosity. For isotropic structures as sandstone and ordinary cement paste, percolation probabilities provide the topological information required [10]. This leads to connectivity functions related to effective properties of cementitious materials.

Network models [13] are idealized representations of the complex pore geometry that may be used to estimate effective hydraulic properties of porous media. It has been demonstrated to be an efficient tool to investigate the effect of geometrical aspects on the effective behaviour of porous media. A network model can be generated on the basis of the aforementioned connectivity function and pore size distribution, which mimics the pore structure in terms of pore size and topology. Vogel and Roth [14] successfully applied network modelling to clay soil and predicted hydraulic conductivity and water retention characteristic (pressure-saturation relation) of the soil. The present authors have explored local percolation probabilities [8] (related to connectivity function) and size distribution of pore structure [5] in cement pastes, but their quantitative correlation to effective hydraulic properties of the materials remains to be solved. This quantitative simulation approach by means of pore network modelling to hydraulic properties of cementitious materials is an interesting and promising aspect for future research.

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