Size Characterisation of Pore Structure for Estimating Transport Properties of Cement Paste

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The conventional experimental approaches to assessing pore structure characteristics (e.g. mercury intrusion porosimetry) in cement paste have difficulties in providing reliable results. This problem can be approached by geometrical statistical and mathematical methods, e.g. stereological analysis and mathematical morphological measurements. This paper deals with the application of these methods to section images of cement paste specimens and presents a representative set of results of size characterization of pore structure in cement pastes with various water cement ratios and degrees of maturity. The size characterization of pore space allows direct prediction of paste permeability with empirical relationships. However, only porosity, pore size, and eventually porosity connectivity (i.e. connected fraction of porosity) are taken into account in the conventional models for estimating permeability of cement pastes, such as the Kozeny-Carman equation and the Katz-Thompson equation. These simplified models cannot provide accurate estimation of paste permeability without significant improvements. Accurate predictions of cement paste permeability and of other transport properties require incorporating information on how the pores are interconnected, i.e., on topology characteristics of pore structure. This requirement can be fulfilled by pore network modelling, which reflects pore size distribution and the complex situation of connectivity in pore space. Potential applications of mathematical morphology methods for constructing the pore network model and thereby estimating transport properties of cement paste are also discussed in this contribution.

Key words: Size characterisation, pore structure, transport properties.

1 Introduction

Details of pore structure are of paramount importance for 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 by 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 information on material structure.

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 [Underwood, 1968] allows deriving three-dimensional (3D) structural information including volume fraction of porosity and specific surface area from two-dimensional (2D) 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 geometrical statistical and mathematical methods to size characterization of pore structure, and with its potential for estimating transport properties of cement paste by means of pore network modelling.

This approach was introduced by Fatt [1956] and subsequently developed in different fields of material sciences. As a morphological representation of the pore structure, pore network modelling has been used in soil technology [Vogel and Roth, 2001] and petroleum engineering for estimating hydraulic properties of porous media. Relevant to concrete technology, a similar method has been applied by Ye [2003] to model cement paste based on the serial sectioning technique. The pore network model is constructed from pore size distribution and topological characteristics of pore structure. The structural information can be obtained easily for model cement paste, although sometimes by time-consuming algorithms. However, in the case of actual cement paste, only 2D sections are available for direct observation and for quantitative image analysis. Note that thin sections provide projection images that could be available too; their suitability for providing information on material structure will not be discussed in this contribution however. The serial sectioning technique is obviously not applicable due to its labour intensive nature. The latter part of this paper discusses application of mathematical morphology methods to section images of cement paste specimens for deriving the structural information necessary for generating network model, and explores the potential application by means of pore network modelling for predicting transport properties of cement paste.

2 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 2D observations. Analogue as well as binary images (with pore space as phase of interest) of specimen sections can be subjected to quantitative image analysis. The pore areas observed on section images are defined as pore features. Stereological theory allows straightforward measurement of volume fraction of pore space, i.e. porosity (ϕ) from section images since area fraction of pore features (i.e. area porosity) is an unbiased estimator of

volume porosity, i.e. $V_V = \overline{A_A}$. The bar on top of the parameter indicates an averaging procedure. 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 μm^{-1}) can be assigned 3D stereological character via the relationship [Underwood, 1968], $s = 4\overline{L_A}/\pi$, where s is the surface area of pore space per unit test volume (expressed in μm-1). For convenience purposes, the stereological parameter - specific surface area (S_V) is replaced by s. 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 (defined as average of uninterrupted distance between solid clusters, denoted as λ in μm) 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 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, mean intercept length can be expressed in porosity and specific surface area by $\overline{L_3} = 4(1-\phi)/s$. The porosity, specific surface area, average pore size and average pore spacing represent basic characteristics of pore structure.

3 Mathematical morphology measurements

3.1 *Two-point correlation function*

Two-point correlation function (TPCF) [Serra, 1982] 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. The integers x and y represent the horizontal and vertical coordinates of a pixel with $1 \le x \le x_{max}$ and $1 \le y \le y_{max}$ (x_{max} and y_{max} are the image dimensions in pixels). 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

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

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 ϕ 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 γ 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 for $r \rightarrow 0$ [Serra, 1982]

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

Dullien [1992] 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. 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. Using SEM (scanning electronic microscopy) on thin sections of sandstone, Berryman and Blair [1987] found that s and, to a lesser extent, ϕ increased with magnification. This is in fact a matter of fractality. Ultimately, ϕ is bounded by total porosity, but significant increase of s at increasing magnification should result in much smaller values of R_{hv}. They reasoned that pore-wall features smaller than 1% of the radius of a characteristic pore size do not significantly affect flow. This in turn would impose a limit on the maximum magnification necessary for determining hydraulically relevant s from SEM section images.

3.2 ***Opening distribution technique***

Another important mathematical morphology measurement for size characterization is the so-called opening distribution [Scrivener, 1989; Hu and Stroeven, 2003]. It is a size classification of pore space based on series of morphological opening operations by structuring elements of increasing size. The traditional approach to deriving pore size distribution from the section image is a direct classification of pore features according to their areas. Linear size parameters are also available in stereological literature for this purpose. These characterization methods based on individual pore features do not make much sense in view of the complex pore network of high tortuosity and connectivity.

4 Application to section images of cement paste

4.1 ***Size characterization***

The authors applied the 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. Fig. 1 shows the pore size distribution curves for cement pastes with w/c of 0.6 at different hydration stages. The opening distribution results are compared with literature data obtained by conventional mercury intrusion porosimetry (MIP), by Wood's metal intrusion porosimetry (WMIP) [Willis et al., 1998] and other modelling approaches [Ye, 2003]. The comparison study reveals good agreement between the pore size distribution obtained by mathematical morphology and by proper experimental technique, WMIP. The opening distribution data are generally in line with the results of a straightforward measurement of pore size distribution for model cement proposed by Ye [2003]. It can be concluded that, in contrast to the conventional method yielding area histograms, the opening distribution technique can provide appropriate characterization of pore size distribution.

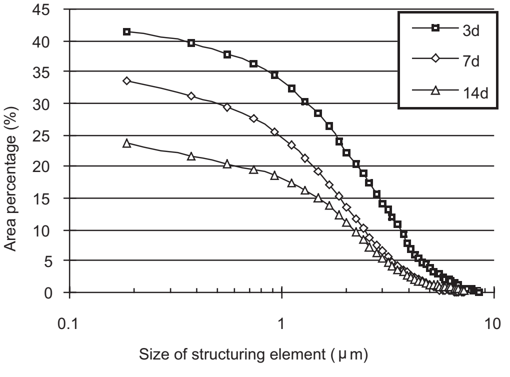

Figure 1: Pore size distribution (opening distribution) curves for cement paste with w/c ratio of 0.6 at 3, 7, 14 days of hydration, respectively.

The morphological evolution during hydration of pore space can be analysed on the basis of the mean free spacing λ (i.e. average pore size). It can be expected to be a monotonously decreasing function of hydration time (Fig. 2). According to the simulation study by the present authors, the depercolation threshold of capillary porosity can be associated with a value of porosity whereby mean free spacing (distance) arrives at a stable value, as shown in Fig. 2. The simulation results reveal a depercolation threshold of 21~23% for cement pastes with ordinary fineness level (such as C342 in Fig. 2). Finer cements have a higher value of depercolation threshold as a result of the higher hydration rate and the smaller inter-particle spacing, which make it easier for finer cement to close off the pore space. The depercolation threshold values are 31.8% and 7.9%, respectively, for cements C605 and C167 in Fig. 2. It is found that particle size distribution exerts significant influences on the depercolation threshold, whereas the effect of w/c ratio is only minor [Hu and Stroeven, 2005a]. The results obtained by this morphological approach are consistent with simulation results of Bentz et al. [1999], as well as with experimental findings of Parrott et al. [1984] and Powers et al. [1959]. The relevance of studying the depercolation phenomenon is given by the close relationship between this parameter and transport phenomena in cement-based materials.

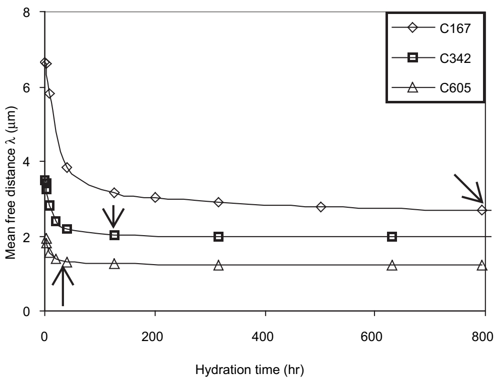

Figure 2: Determination of the depercolation threshold of porosity by a morphological approach: the depercolation threshold is associated with the porosity value whereby the mean free distance decreases to a stable end value during the hydration process. The depercolation threshold points are indicated with arrow. The cement samples are coded according to their Blaine specific surface area values (in m^2/kg).

Another important size characterization is based on the so-called critical pore size l_c (in µm). 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; see [Hu and Stroeven, 2003] for details. Supposedly, this is a monotonously decreasing function of hydration time for a given cement paste. The well-known Katz-Thompson [Katz and Thompson, 1986] equation is based on porosity and critical pore size data.

*4.2 **Characteristic length scale and size characterization***

TPCF is also instrumental for obtaining statistics of material microstructure, and that have been used to estimate fluid permeability of soils [Schaap and Lebron, 2001] and sandstones. The readers are referred to the authors' publication elsewhere [Hu and Stroeven, 2002] for the application of various mathematical morphology measurements to size characterization of cement paste. It should be noted, however, that the size characterization approach by Berryman and Blair [1987] 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 ϕ^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. However, 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 a certain bulk property. The calculated R_c values

are 2.4, 2.6 and 3.1 μm for cement pastes (w/c=0.5) at increasing hydration time (3, 7 and 14 days, respectively). This is corresponding to the increasing size of the RAE for porosity distribution with maturing cement pastes [Hu and Stroeven, 2005b].
Hydration induces continuous changes in the cement microstructure, yielding an RVE for more matured cement paste exceeding in size the one for early-age cement. When a comparison study would be based on similar volume (or area) elements, heterogeneity in the same type of parameter would, as a result, increase as a function of hydration time. The present authors explored the statistical concept of heterogeneity in cement paste, and its implications for size sampling strategy in comparison studies of evolving pore structure in cement pastes on the basis of an upgraded approach of local porosity theory that is originally proposed by Hilfer [Hilfer et al., 1997]. Fig. 3 present the local porosity distribution curves for a cement paste at different degrees of maturity. When based on constant field size *L* (i.e., linear dimension of the measurement unit in which porosity is measured and defined as local porosity), more matured cement paste (with 14 days of hydration) indicated a much wider distribution curve than younger samples (with 3 and 7 days of hydration), corresponding to a higher degree of heterogeneity for local porosity distribution (Fig. 3). Hence, R_c is obviously not a size characterization of pore structure, since average pore size is *decreasing* during the hydration process. Pore size can be assessed properly by the mean free spacing or by the correctly defined hydraulic radius.

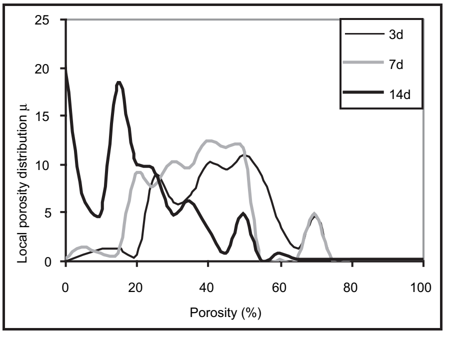

Figure 3: Local porosity distribution m for cement paste with w/c=0.6 at 3, 7 and 14 days of hydration, respectively, at constant linear field size L=19 μ.

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 unit in local porosity analysis and lag in TPCF). Biswal et al. [1998] employed the local porosity theory to analyse local porosity distribution (μ) in different sandstone samples. They defined a characteristic length scale as the minimum linear dimension of measurement cell (L^*) when the μ curve vanishes at both ends of porosity-axis (porosity equal to 0 and 1, respectively). They compared the μ curves of different sandstones at their respective values of L^* and associated the width of the curves with heterogeneity of sandstones. This approach is incorrect because L^* defined in [Biswal et al., 1998] is equal to average pore spacing. When the measurement cell is large enough to cover at least two pore features (i.e., when linear dimension of the measurement cell is larger than average pore spacing), the μ curve will present zero values at both ends of the porosity-axis, since it is impossible for the measurement cell to cover exclusively pore space or solid phase. For example, the average pore size and the average pore spacing are 3.7 and 13.3 μm for the cement paste with w/c=0.6 at 14 days hydration. When the field size is between the average pore size and the average pore spacing, the μ curve will present non-zero value at porosity=0 end but vanish at porosity=100% end, sine it is nearly impossible for a field of this size to be encompassed in pore space, while possible to be encompassed in solid phase. This is explicitly confirmed by the curve with L=9 μm in Fig. 4. When the field size exceeds the average pore spacing to a certain extent, the field will explore at least two pore features, hence, the μ curve will vanish at both ends of the porosity-axis (Fig. 4). Hence, L^* defined by Biswal et al. has no direct correlation with the length scale of the RAE. Based on the statistical concept of heterogeneity, the characteristic length scale should be assessed by the minimum length of measurement cell whereby the local porosity distribution conforms to the normal distribution function. In a comparison study on cement pastes with different w/c ratios and different degrees of maturity, the length scales used for different paste samples should be maintained at fixed proportion to the sizes of their respective RVE/RAEs to ensure a comparison on similar level of the microstructure (i.e. a similar coefficient of variation of the parameter at issue) [Hu and Stroeven, 2005b]. The long-range fluctuation behaviour of correlation functions observed in a study of Schaap and Lebron [2001] for soil structure can also be associated with size characterizations.

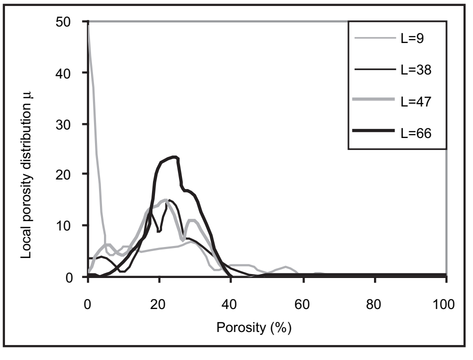

Figure 4: Local porosity distribution μ(ϕ, L) for cement paste with w/c=0.6 at 14-day's hydration, at linear probe sizes L of 9, 38, 47 and 66 μm, respectively.

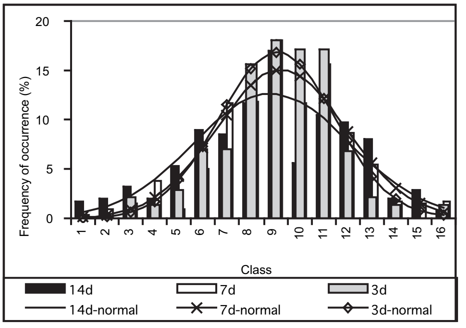

Figure 5: Histograms of frequency of occurrence in porosity distributions for the same pastes as in Fig. 3 but in this case, field sizes were proportional to the respective RAE sizes, i.e., the comparison is made on similar level of the microstructure. The experimental values are indicated as columns and the approximated normal distribution curves are shown as continuous lines.

5 Potential for estimating transport properties

5.1 ***Empirical equations for estimating permeability***

The size characterization allows estimating water permeability k of cement pastes by means of some empirical relationships. These equations require structural information encompassing porosity, pore size (hydraulic radius) and pore geometry. The present authors studied the applicability of two frequently used models, i.e., Katz-Thompson equation and Kozeny-Carman equation [Carman, 1939]. The latter model provides quantitative relationship between permeability and porosity, hydraulic radius and tortuosity of the transport path in cement paste. Both equations have been proved to offer satisfactory estimation of permeability for sandstones and soils. However, the applicability cannot be readily extended to cement paste without significant modification.

Christensen et al. [1996] employed the Katz-Thompson equation to predict the water permeability of cement pastes in high w/c range (above 0.47) and argued that the Katz-Thompson model provided reliable estimation. However, the error of prediction increases dramatically in the case of the lower w/c range, especially for more mature conditions. Overestimation by the Katz-Thompson equation is striking, usually more than two orders of magnitude. A better approach in this case is the so-called General Effective Media theory [Cui and Cahyadi, 2001; Hu and Stroeven, 2003]. Schaap and Lebron [2001] 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. Herein, they formulated a proposal for upgrading the Katz-Thompson relationship on the basis of effective characterization of pore morphology, by incorporating a new stereological parameter, the so-called pore distribution density Γ_{3D}. It is a 3D parameter obtained from section image analysis on the basis of stereological theory, containing information about pore size and pore connectivity. The strongest correlation with k is found to occur for Γ_{3D}, followed by critical pore size l_c and porosity p. The integration of Γ_{3D} into Katz-Thompson equation therefore largely improves the prediction capability of this method [Hu and Stroeven, 2004].
This implies that accurate predictions of cement paste permeability and other transport properties require incorporating information on how the pores are interconnected, i.e., topology characteristics of pore structure. Vogel [1997] 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 accurate prediction of paste permeability. This requirement can be fulfilled by pore network modelling [Fatt, 1956], which is constructed on the basis of pore size distribution and pore topology characteristics.

*5.2 **Application of pore network modelling***

Ye [2003] constructed a network model on the basis of serial sectioning of model cement paste. Detailed information on pore features were extracted from closely spaced serial sections whereby the centre of each pore feature was considered as a node. An overlapping criterion was then used to determine the detailed situation of connection between nodes on neighbouring sections; each link between these neighbouring nodes was defined as a branch. In this way, a linked list network is formed. The method of Ye yielded satisfactory prediction of paste permeability compared to experimental measurements, as long as the minimum size of cement particles is small enough (1 μm or smaller) to approximate the realistic situation in cement production. This implies that the prediction accuracy is largely dependent on whether the cement simulation is sufficiently realistic.
However, this straightforward method is not applicable to actual cement paste due to the extreme labour intensity. Mathematical morphology tools can be used in this case to derive the structural information on pore size distribution and on pore topology that are necessary for constructing a pore network model. The application of mathematical morphological methods to structural analysis discussed earlier in this paper deals with only a small part of pore structure characterization. The application of mathematical morphology can be extended to more complex morphological aspects of materials, such as pore topology, pore network modelling and simulation of effective hydraulic properties. For an isotropic structure like ordinary cement paste, one single properly sampled section or a few sections can provide reliable information, provided the size of the sampled area is representative for the investigated parameter. This

prevents appealing to serial sectioning, requiring dramatically high labour investments. On the other hand, the direct applicability to section images of specimens extract the structural features of actual cement paste, thus being independent on quality of computer simulation.

5.3 ***Construction of pore network model***

Network models are idealized representations of the complex pore geometry that may be used to calculate effective hydraulic properties of porous media. Network modelling has been demonstrated to be an efficient tool for investigating the effects of geometrical aspects on the effective behaviour of porous media [Friedman and Seaton, 1996]. Vogel and Roth [2001] successfully applied network modelling to clay soils and predicted hydraulic conductivity and water retention characteristics of the soils. Comparison of simulation outcomes with experimental results reveals good agreement, indicating the hydraulic properties to be mainly governed by pore size distribution and topology. Hence, a simple network model can be generated and adapted to a predefined pore-size distribution and connectivity function. It should be noted that the term 'connectivity' employed in [Vogel and Roth, 2001] does not mean the volume fraction of connected porosity (i.e. porosity connectivity), but is defined as the number of redundant connections (also referred to as genus number in mathematical morphology [Serra, 1982]). This connectivity is increasing as hydration proceeds, since the pore structure changes from a wholly connected pore space to a very complex network composed of isolated pores, dead-end pores and effective pores. Vogel and Roth [2001] concluded that pore topology can be characterized to a satisfactory extent by the so-called connectivity function. Besides porosity and pore size distribution, the topology of pore space is a crucial property regarding flow and transport in porous media. The Euler characteristic combines the basic topological measures (*i.e.,* number of isolated pores, number of redundant connections, number of enclosed cavities) into a measure of connectivity. The Euler characteristic may be deduced from the local geometry of the structure without explicitly counting the basic topological measures [DeHoff, 1987]. This is of practical importance in cement paste technology, since a full 3D representation is hard to get. In the context of mathematical morphology, a connectivity function can be derived from measurements of the Euler characteristic as a function of pore size [Vogel, 1997]. Starting with the largest pores that may be isolated and not connected, the smaller pores are successively added, which change the topology in a characteristic way, i.e., accompanied by an increase in connectivity. This imaginary process of adding pores successively to the pore network is associated with the definition and determination of critical pore size. The connectivity function yields an integral description of the overall topology and should reflect the hydraulic behaviour of cementitious materials because it contains information on how pores of different sizes are interconnected.

Another approach towards the quantification of topology in porous media is the measure of percolation probability denoting the probability to find a continuous path through a sample of a given size. Percolation probability 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 [Hilfer et al., 1997]. Fig. 6 presents the local percolation probabilities for a cement paste in different directions, see [Hu and Stroeven, 2005b] for details. $\lambda_3=1$ indicates the sample is fully connected in all *x, y* and *z* directions. λ_1 presents the percolation probabilities in at least one of these directions. $\lambda_0=1$ is corresponding to a blocking sample. This leads to connectivity functions related to effective properties of cementitious materials.

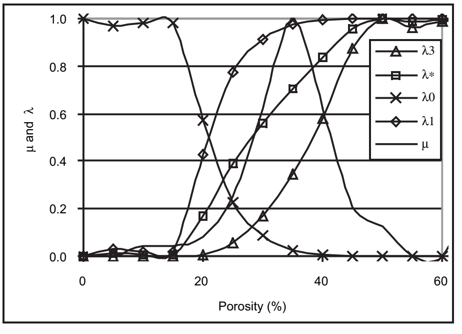

Figure 6: Local porosity distribution m and local percolation probabilities λα for cement paste with a w/c=0.4 at 3 days hydration, at the characteristic length scale L=40 μ; λ represents the local percolation probabilities in x, y and z direction ($\lambda_x=\lambda_y=\lambda_z$).*

The network model can be generated on the basis of aforementioned connectivity function and pore size distribution, which mimics the pore structure in terms of pore size and topology. The present authors explored the local percolation probabilities [Hu and Stroeven, 2005b] (related to connectivity function) and size distribution of pore structure [Hu and Stroeven, 2003] in cement pastes, but their quantitative correlation to effective hydraulic properties remains to be solved. This requires application of pore network modelling on the basis of pore size distribution and topology. The quantitative simulation approach by means of pore network modelling to transport properties of cementitious materials is an interesting and promising tool for future research.

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