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Fractal modelling of medium–high porosity SiC ceramics

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Abstract

A fractal model (denominated IFU) is presented, developed by varying some constructive aspects of Menger sponge. Simple fractals can be used effectively to describe pore size distributions which present a regular growth toward the larger diameters and therefore are not suited to the description of very common structures which present one or more peaks in the distribution. The use of more fractal units means that the IFU is able to simulate effectively the pore size distribution, the volume fractions of the voids and the geometry of the microstructure. The modelling is applied to sets of published data regarding SiC based ceramics characterised by a medium–high volume fraction (40%/80%), obtained through the technique of mercury intrusion porosimetry. Finally, this study demonstrates how the permeability can be realistically estimated based on the parameters of the proposed model.

Keywords: Fractal geometry; Porosity; SiC; Sintering

1. Introduction

In characterising porous materials, a description of the geometry of the system of voids and their simulation with suitable models is a preliminary phase in the correlation of the physical and technical characteristics, particularly permeability. The use of Fractal Geometry has recently been established in this sector,[1–3] but the adoption of "simple models", the most noted of which is effectively exemplified by Menger sponge[4] presents two problems: the succession of the pore sizes which count only a few terms for every decade and the distribution of the volumes concentrated towards the class of larger pore diameters.

This study demonstrates how the use of a series of interconnected fractal units (Intermingled Fractal Units, IFU) can bring about an effective representation of the porosimetric characteristics of SiC based ceramics of medium to high porosity, produced using a variety of techniques.

The industrial production of SiC dates back more than 100 years. At first this was prevalently concentrated on exploiting its "diamond-like" hardness and successively the refractory characteristics of this ceramic compound.[5] In recent years this material's many excellent characteristics have become the subject of much research and industrial exploitation. Stability at high temperature, and the resistance to aggressive fluids lead to the development of SiC with porosity of between 40% and 80%. This is now of particular interest in the production of filters, catalysts or heat accumulators.[6–10]

The experimental porosimetric data used in the following treatment are derived from the literature.[9,10] They were obtained by the technique of mercury intrusion porosimetry (MIP).

2. Basic concepts of the application of fractal geometry in materials

In the last decades a geometry has been developed which refers to figures with fractional dimensions, so called fractals, term derived from the Latin *fractus*.[4]

"Roughly, dimension indicates how much space a set occupies near to each of its points, ... it is a measure of the prominence of the irregularities of a set when viewed at very small scales, ... the dimension reflects how rapidly the irregularities develop, ..."[11] According to Mandelbrot, the importance of this approach to irregular figures is owed to the fact that it is particularly well adapted to the description and analysis of a large number of natural forms.[4] In particular, a deterministic fractal is a geometric figure, every part of which is similar of the whole, replicated on different scales and so it is expressed by a power law. Some researchers have, utilising these concepts,

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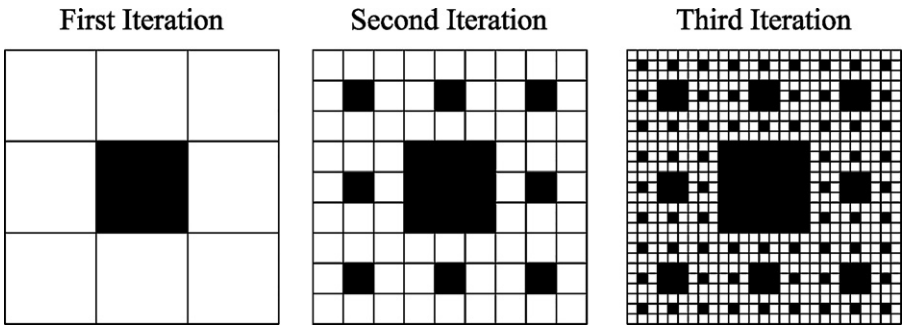

Fig. 1. Example of fractal construction: Sierpinski carpet as a simple model of cross section porosity.

discovered that also different aspects of the microstructure of materials can be considered to be fractal.

As an example of a fractal we can cite the lines and the surfaces of cracks which owing to their strongly irregular character, and on diverse dimensional orders of magnitude, have been described as "curves" or "surfaces" with dimensions comprised between 1 and 2 (1 being Euclidean) and 2 and 3 (2 being Euclidean).[12,13] With regard to porosity, Fractal Geometry presents us with a series of well known figures or "sponges" which although simple, in their formulation and appearance they call to mind the distribution of pores, for example Sierpinski carpet, fractal dimension = 1.89, Fig. 1, or the corresponding three dimensional model known as Menger sponge, fractal dimension = 2.73.[4]

The porosimetric data, obtained with the noted mercury intrusion or gas absorption techniques, can be processed in fractal terms with the development of a scaling procedure, self similarity, on at least two or three orders pores dimension magnitude. The determination of fractal dimension value (D_f) will be done, e.g. with Pfeifer and Avnir[14] approach: let v and r are the pore volume and radius, respectively, we can write the power law $(-dv/dr) \propto r^{2-D_f}$. The applications which have already been reported in literature are numerous and include: cement materials, sandstones, soils, and also traditional and advanced ceramic materials.[15] Moreover, it has even been possible to attach to the geometrically fractal representation an effective and rational, not empirical, estimate of physical greatness which are technologically as relevant as the permeability to fluids or the coefficient of heat transmission of porous materials.[1,16]

3. The intermingled fractal units (IFU) model

One of the most noted models for fractal porosity is the Menger sponge. Even though it expands infinitely, in practice it is evidently necessary to take into consideration just the dimensional range of the pores of the materials considered. In this way, if the voids distribution of a particular porous microstructure develops, or is experimentally determinable, between two limits (Λ is the superior) Menger sponge will be made up of a unit represented by a cube of side $L_0 = 3\Lambda$ and with a succession of pores of dimension Λ, $\Lambda/3$, $\Lambda/9$, …, $\Lambda/3^i$, …. For example if $\Lambda = 10\,\mu m$ the succession of the pore sizes characterising the microstructure will be: 10, 3.3, 1.1, 0.37, 0.12, 0.04, … μm (two apertures for every decade). The fractal dimension D_f and the voids fraction ε for these structures are:

$$D_f = \frac{\log (N^3 - N_s)^i}{\log (N)^i} \qquad \varepsilon = 1 - \left(\frac{N^3 - N_s}{N^3}\right)^i,$$

with N being the number of divisions of the side and N_s the number of sub-cubes subtracted at every iteration i, concerning all of the $N^3 - N_s$ sub-cubes. In the previous example, with $N = 3$ and $N_s = 7$ it has a $D_f = 2.727$, and with $i = 8$ it has $\varepsilon = 0.91$. The pore size distribution assigns the maximum value of the volume, 26%, to the pores with sides of 10 μm.

A first modification on the fractal model of Menger can be finalised to acquire a larger capacity of simulation; it predicts that only some sub-cubes are iterated (N_{unit_iter}), while others are excluded from the process (N_{sfe}). In this case the D_f and the ε are:

$$D_f = \frac{\log N_{unit\_iter}}{\log N} \qquad \varepsilon = \sum_i \left[(N_{unit\_iter})^{i-1} \cdot \frac{N_s}{(N^3)^i}\right].$$

Furthermore, the necessity of having a model characterised by a large number of pore sizes for every decade obliges us to use jointly more fractal units, FU, characterised by different values of Λ, and the different FU do not necessarily have to have the same D_f.

The global model is finally assembled by intermingling a number n of each of the FU. It is presumed that such values that largely determine the volume of the pore size classes must be very high.

From Darcy's and Hagen–Poiseuille's relations, assuming that $N = \Lambda^{D_f}\lambda^{-D_f}$ and $L = (L_0)^{D_t}\lambda^{1-D_t}$, respectively, the number and the length of pores as in references[1,3] and where λ is the generic pore size and D_t is the so called fractal dimension for tortuosity ($1 \le D_t \le 2$, $D_t = 1$ is equivalent to a bundle of straight channels, $D_t = 2$ corresponds to a so highly tortuous patterns that fills a plane), the expression for the permeability k of every FU is:

$$k_{FU} = \left(\frac{\pi}{128}\right) \cdot \left[\frac{(L_0)^{1-D_t}}{A}\right] \cdot \left[\frac{D_f}{3 + D_t - D_f}\right] \cdot \Lambda^{3+D_t},$$

where A is the total sectional area (for a Menger unit is $A = 3^2\Lambda^2$). In the model proposed we can write D_t (in the plane) = D_f (in the space) − 1, consequently:

$$k_{FU} = \left(\frac{\pi}{256}\right) \cdot \left(\frac{D_f}{3^{D_f}}\right) \cdot \Lambda^2.$$

Finally, the k of the (global) model can be expressed as an average with respect to the volume fraction occupied by various FU. The number of FU has been established by trial and error method, minimizing the difference between ε and pore size distribution calculated and experimental.

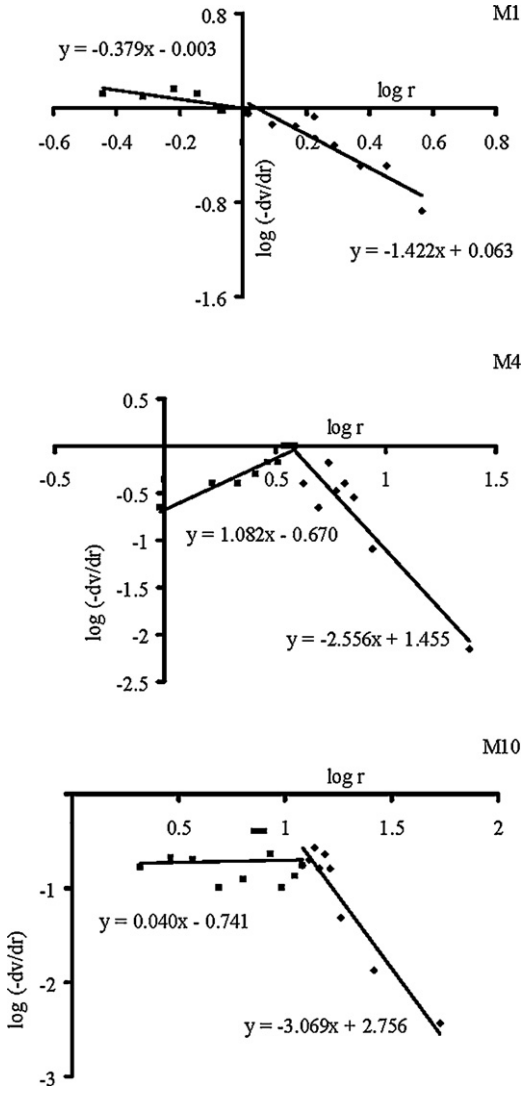

Fig. 2. Log–log plot of the MIP experimental data of ceramics M1, M4 and M10.

Table 1
The parameters of the IFU models (with 3 fractal units) for M1, M4 and M10

	M1	M4	M10
FU1			
Λ, μm (n)	22 (1)	38 (1)	75 (1)
D_f (N_{sfe})	2.40 (1)	2.26 (12)	2.10 (12)
FU2			
Λ, μm (n)	15 (1)	26 (3)	55 (5)
D_f (N_{sfe})	2.40 (13)	2.26 (12)	2.10 (13)
FU3			
Λ, μm (n)	1 (37k)	3 (30k)	5 (80k)
D_f (N_{sfe})	2.40 (13)	2.26 (15)	2.10 (15)
$\varepsilon_{calc}/\varepsilon_{exp}$	0.80/0.78	0.89/0.86	0.82/0.80
k ($\times 10^{13}$ m^2)	2.49	3.13	11.8

4. Results and discussions

Pore size distributions with a bell-like form, and therefore with a unique peak value, characterise the samples of high porosity SiC discussed in reference.[9] Data relative to three systems were processed, with pore size corresponding to the maximum volume distribution of 1, 4 and 10 μm (Figs. 4–6 of reference[9]), herein referred to as M1, M4 and M10. According to Pfeifer and Avnir procedure, the MIP experimental data are correlated with two distinct straight lines which intersect in correspondence with the peak of the distribution, as reported in Fig. 2. According to the current interpretation, the gradient (m) of these straight lines would be connected to the fractal dimension of the porous microstructure ($D_f = 2 - m$). In our case the "D_f" values range from 1 to 5, therefore none of the materials have a D_f definable

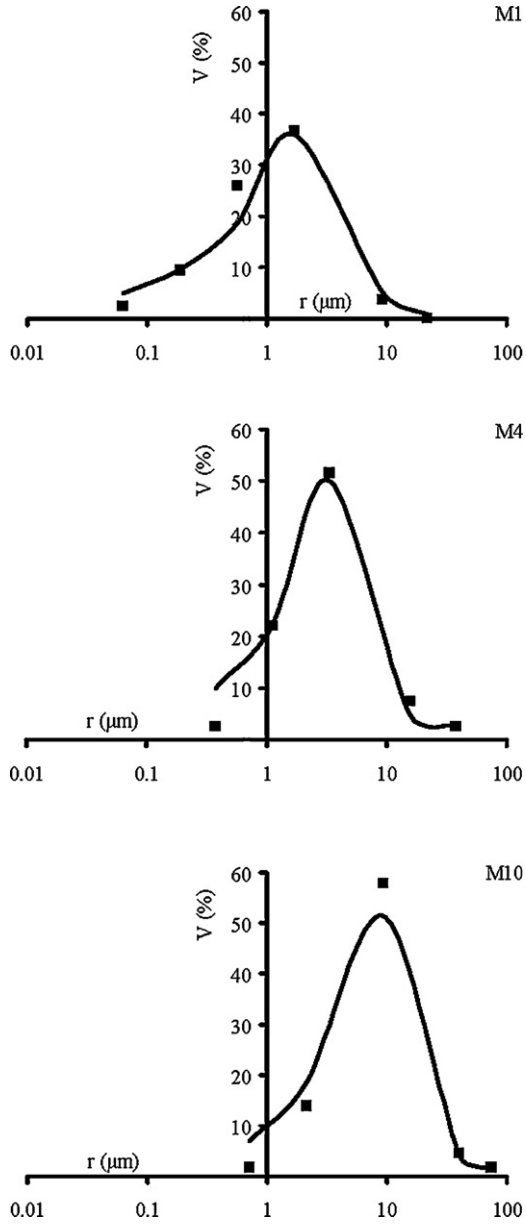

Fig. 3. Pore size distributions; experimental (points) and derived from the model (curves) for the ceramics M1, M4 and M10.

as legitimate ($2 \leq D_f \leq 3$) so one must conclude that their pore size distribution cannot be considered fractal.

In the modelling, it is convenient to select pore sizes which have a precise order; this study presents the rationality and efficiency of a procedure based on the combination of fractal units. For the cases in question three units were adopted, referred to herein as FU1, FU2 and FU3, and Table 1 displays their characterising parameters. In the construction of the model every FU is repeated a number of times. For example, the simulation of the porous microstructure of M4 is made up of the intermingling of one FU1 with $\Lambda = 38\,\mu m$, three FU2 with $\Lambda = 26\,\mu m$ and thirty thousand FU3 with $\Lambda = 3\,\mu m$; with the D_f equal to 2.26. The thirty thousand units of FU3 occupy a global volume of around fifteen times that occupied by one unit of FU1. The number of pore diameters between 38 μm and around 2 nm is 26. Table 1 displays the concordance between the volume fraction of voids, experimental and calculated from the model, while Fig. 3 shows its capacity for simulating the pore size distribution as well.

Other researchers obtain medium porosity SiC with a pore size distribution characterised by the presence of more peaks. The ceramics of reference[10] which we have considered are those defined by the temperature of sintering of 1800, 1850, 1900 and 1950 °C henceforth referred to as E80, E85, E90 and E95. Also in this case, a true fractal dimension is not definable for the experimental data reported in the log–log plot (Fig. 4). Nevertheless, the simulation of the microstructure can still be accomplished by a series of intermingled fractal units. Table 2 presents the parameters of the models, with five FU, and values of ε. Notwithstanding the enormous difference between the number of the various units employed in the construction of a global model it is found that the volumes of the n FU are of the same magnitude.

Table 2 demonstrates the accord between the volume fraction of voids, experimental and calculated from the model, while

Table 2
The parameters of the IFU models (with 5 fractal units) for systems E80, E85, E90 and E95

	E80	E85	E90	E95
FU1				
Λ, μm (n)	30 (1)	30 (1)	30 (1)	30 (1)
D_f (N_{sfe})	2.89 (2)	2.89 (2)	2.89 (2)	2.89 (2)
FU2				
Λ, μm (n)	28 (5)	28 (5)	28 (3)	28 (3)
D_f (N_{sfe})	2.93 (1)	2.85 (3)	2.73 (1)	2.93 (1)
FU3				
Λ, μm (n)	3 (3k)	3 (4k)	3 (1.8k)	3 (1.4k)
D_f (N_{sfe})	2.10 (17)	2.40 (13)	2.18 (15)	2.26 (15)
FU4				
Λ, μm (n)	0.3 (11M)	0.3 (20M)	0.3 (3.3M)	0.3 (1.7M)
D_f (N_{sfe})	2.10 (12)	2.10 (8)	2.40 (13)	2.33 (10)
FU5				
Λ, μm (n)	0.1 (110M)	0.1 (100M)	0.1 (150M)	0.1 (300M)
D_f (N_{sfe})	2.97 (1)	2.97 (1)	2.97 (1)	2.97 (1)
$\varepsilon_{calc}/\varepsilon_{exp}$	0.56/0.53	0.47/0.51	0.42/0.43	0.39/0.35
k ($\times 10^{13}$ m^2)	2.93	2.22	3.19	2.39

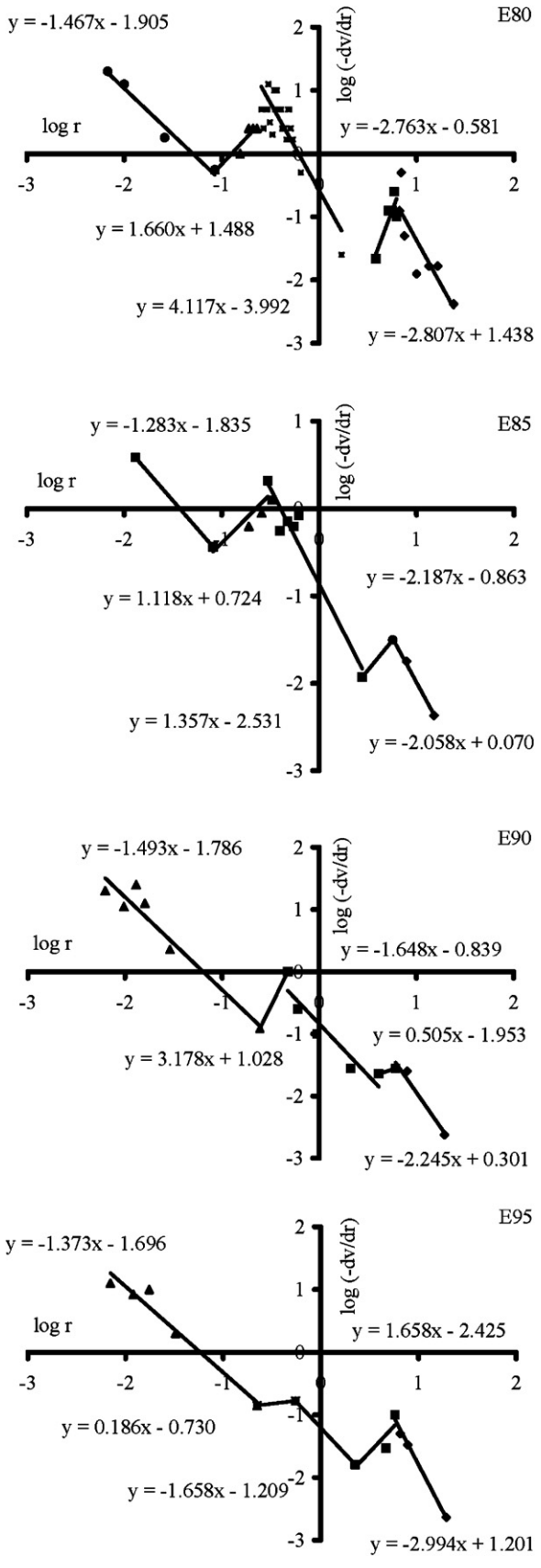

Fig. 4. Log–log plot of the MIP experimental data of the ceramics E80, E85, E90 and E95.

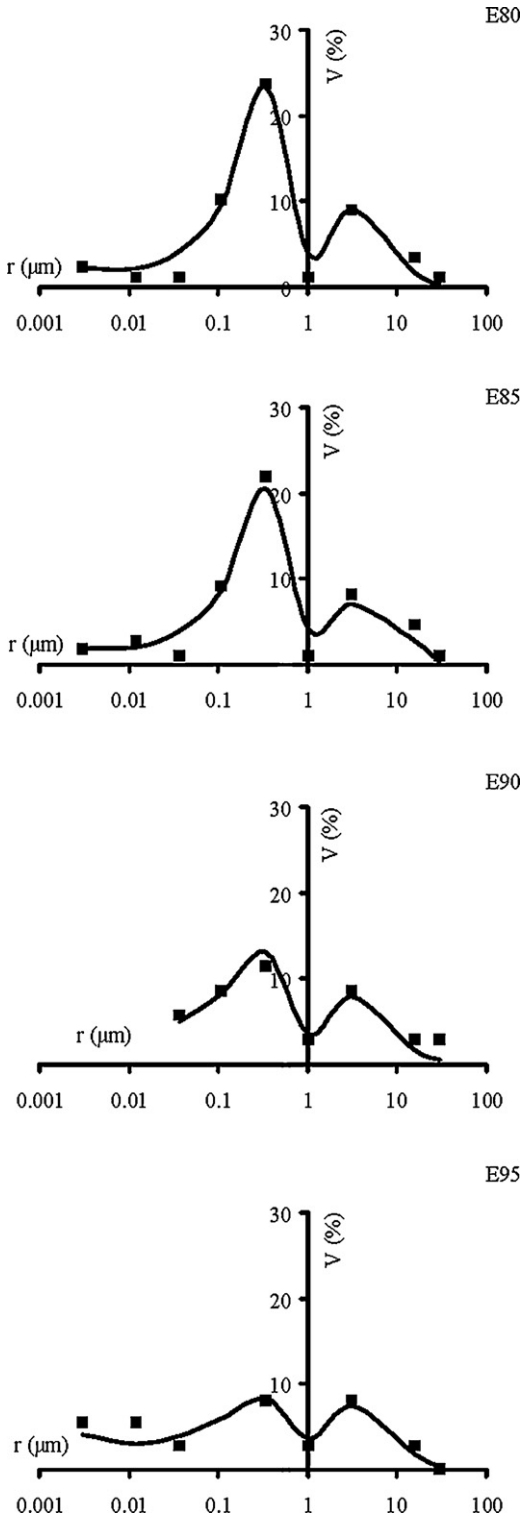

Fig. 5. Pore size distributions; experimental (points) and derived from the model (curves) for the ceramics E80, E85, E90 and E95.

Fig. 5 displays the capacity of this to simulate the pore size distribution.

The permeability values calculated on the IFU model are reported in Tables 1 and 2. The permeability values of M1, M4 and M10 are regularly rising with the pore dimensions corresponding to the maximum of distribution. Instead, the k of E80, E85, E90 and E95 are all similar. This is probably linked to the role played by the larger pores, whose fractions are only slightly altered during sintering. The values calculated are substantially in agreement with data reported in the literature, e.g. in references[17,18] for ceramic materials with similar porosimetric characteristics.

5. Conclusions

The use of a fractal model is capable of rigorously describing only those microstructures which can be effectively approximated by a model which predicts a regular growth of the distribution towards the extreme of the largest diameters. A pore size distribution with one or two peaks, frequently found in practice, cannot be representative of a true fractal because the volume–size of the pores is missing from the characteristics of scaling on the data.

The pore size distribution considered in this study regards SiC based ceramics of a medium–high porosity. The representation of MIP experimental data in the form of a $\log(-\mathrm{d}v/\mathrm{d}r)$ vs. $\log r$ according to the procedures of Pfeifer and Avnir, exclude however that a true fractal dimension can be derived.

Moreover, it is possible to obtain from the linear correlation on the log–log plot, regarding both the experimental data and the results from the models, "good" fitting, which gives apparently satisfactory results if the geometric implications are not considered. It is possible that in the literature, situations of this genre have led to the presumption of the existence of a fractal character, with the adoption of the concept of a "mean" fractal dimension, even when, in reality, this is strongly doubted.

However, notwithstanding that the experimental distributions are not recognisable as fractal, their simulation with intermingled fractal units proved to be very effective in giving a value of volume fraction of voids and of their dimensional distribution very similar to the experimental results. The utility of this model is demonstrated by considering that the values of permeability calculated are in agreement with the experimental data of homologous systems.

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