Characterization of the pore structure of reservoir rocks with the aid of serial sectioning analysis, mercury porosimetry and network simulation

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Abstract

Processes of fluid transport through underground reservoirs are closely related with microscopic properties of the pore structure. In the present work, a relatively simple method is developed for the determination of the topological and geometrical parameters of the pore space of sedimentary rocks, in terms of chamber-and-throat networks. Several parameters, such as the chamber-diameter distribution and the mean specific genus of the pore network are obtained from the serial sectioning analysis of double porecasts. This information is used in the computer-aided construction of a chamber-and-throat network which is to be used for further analysis. Mercury porosimetry curves are fitted to either 2-parameter or 5-parameter non-linear analytic functions which are identified by the median pressures, mean slopes and breakthrough pressures. A simulator of mercury intrusion/retraction, incorporating the results of serial tomography, in conjunction with the experimental mercury porosimetry curves of the porous solid are used iteratively to estimate the throat-diameter distribution, spatial correlation coefficients of pore sizes and parameters characterizing the pore-wall roughness. Estimation of the parameter values is performed by fitting the simulated mercury porosimetry curves to the experimental ones in terms of the macroscopic parameters of the analytic functions. The validity of the pore space characterization is evaluated through the correct prediction of the absolute permeability. The method is demonstrated with its application to an outcrop Grey-Vosgues sandstone.

Keywords: Pore structure; Mercury porosimetry; Pore network; Capillary pressure; Permeability; Network connectivity; Pore size; Fractal dimension; Spatial correlations; Serial tomography

1. Introduction

The microstructural properties of sedimentary porous rocks (e.g. sandstones, limestones, dolomites, etc) influence a variety of transport processes either of industrial interest, such as the oil and gas recovery from rock reservoirs, or of environmental significance, such as the contamination of underground aquifers with seawater, industrial chemicals, agricultural chemicals and landfill leachates, the in situ remediation of contaminated groundwater, etc.

The geometrical and topological properties of the pore structure specify to a great extent the various pore-scale mechanisms of multifluid transport, as for instance, the meniscus motion, the fluid disconnection and redistribution, the hydrodynamic dispersion of miscible liquids, the interfacial mass-transfer, the transport-deposition of colloids, the diffusion and reaction of gas mixtures, etc [15,30,39,45,53]. Mesoscopic transport coefficients of underground reservoirs (e.g. capillary pressure curves, absolute and two- or three-phase relative permeabilities, hydrodynamic dispersion coefficients, electrical formation factor and resistivity index) are complex functions of parameters of the pore structure [7,18,22,32,54], dimensionless parameters of flow rates coupled with physicochemical properties of fluids [2,12,29,57], wettability [6,28,55] and saturation history [15,45]. The transport coefficients of reservoir rocks bridge the gap between the pore scale dynamics of multiphase processes and the spatial/temporal evolution of phenomena at the
macroscopic scale of an oil reservoir or an aquifer [8,17,42].

Optical techniques are widely used for the characterization of the pore structure of relatively macroporous materials such as granular packs, sandstones, soils, etc. Image analysis techniques allow us to determine geometrical properties of the three-dimensional pore space by processing data of two-dimensional random sections [15] with the aid of the principles of quantitative stereology [56], and estimate topological properties of the interconnected pore structure by analyzing data of serial sections [13]. Algorithms of reconstruction of the three-dimensional pore network from data of two-dimensional pore features of serial sections (serial tomography) have been developed for the simultaneous determination of both topological and geometrical properties of porous media [3,26,33,34].

Mercury porosimetry is the fastest method of determining the capillary pressure curves, in which is embedded information about a wide range of pore sizes (equivalent capillary cylindrical diameter from \( \sim 180 \) \( \mu \text{m} \) down to \( \sim 0.005 \) \( \mu \text{m} \)). For this reason, mercury porosimetry is the most important method of analysis of the pore structure for a wide variety of porous materials [15]. The conventional interpretation of capillary pressure data is based on the dubious assumption that the pore space can be represented as a bundle of parallel, non-intersecting cylindrical tubes of equal length but of different diameter [14]. Based on ideas of percolation theory [15,45], several researchers have developed simulators of mercury intrusion/retraction in pore network models, using more sophisticated representations of the pore structure [1,9,18,21,27,36,41,43,49,53]. Such simulators have extensively been used to study the effects of geometrical and topological parameters of pore networks (pore size distribution, coordination number, etc) in the form of capillary pressure curves. Special attention has been paid to the effects of the spatial pore size correlations on the capillary properties of porous media [10,19,37,44,50]. Nevertheless, little progress has been made on the use of the pore network simulators for the solution of the reverse problem of characterization of the pore structure in terms of network models [18,37,38,41,52].

In the present work, a systematic procedure for the characterization of the pore structure of sedimentary rocks such as sandstones, by deconvolving the mercury intrusion/retraction curves is developed. The procedure of combining the data of serial tomography with the analysis of mercury porosimetry data using a pore network simulator of mercury intrusion/retraction is demonstrated in the case of a sample of Grey-Vosgues sandstone. The predictability of the absolute permeability of the porous sample is used for the evaluation of the validity of the estimated microscopic parameter values.

2. Theoretical model of the pore structure

2.1. Pore space connectivity

The topological properties of porous media quantify the network skeleton and are independent of any microscopic details concerning pore shapes and sizes [13,31]. For a porous sample, there are two classes of structural aspects that are reported by the topological properties. These are: (1) the number of disconnected parts of pore network (sub-networks) in the unit volume of the sample, and (2) the total connectivity of the network in the unit volume of the sample. The concept of connectivity of a pore structure, which is a measure of the degree to which the pores are multiply connected, can be most directly understood for a network of points (nodes) and lines (bonds) in space. For such a network composed of \( n \) nodes and \( b \) bonds, the quantitative measure of the connectivity is called the 1st Betti number [13,31], \( p_1 \), and is defined by

\[
p_1 = b - n + p_0,
\]

where \( p_0 \) is the 0th Betti number [13,31], which is equal to the number of disconnected parts of a network. In general, for the examination of the topology of a complex multiply connected closed surface in space, it is useful to introduce the concept of its deformation retract [13,31], which is formed by shrinking the surface continuously until it approaches a bond-and-node network (Fig. 1). In this manner, the 0th and 1st Betti

Fig. 1. A multiply-connected 2D porous structure \( (G_{\text{max}} = 9, G_{\text{min}} = 1) \).
numbers of the deformation retract of a set of closed surfaces correspond to the number and connectivity of the set of surfaces. The serial sectioning analysis of pore structures is based upon forming the deformation retract of the interface separating the solid matrix from the pore space and determining the Betti numbers of this network [33–35,59]. A direct measure of the connectivity of a multiply connected closed surface is the genus. The genus \( G \) of a multiply connected closed surface is defined as the number of (non-self-intersecting) cuts that may be made upon the surface without separating it into two disconnected parts [13]. In practice, the genus of a closed surface (namely, the interface between the pore space and the solid matrix) is numerically equal to the 1st Betti number of its deformation retract [31]. It is possible to put bounds on the estimate of genus for a given sample. These two bounds, \( G_{\text{max}} \) and \( G_{\text{min}} \) are determined by taking into account and ignoring, respectively, in the calculations, the bonds crossing the sample boundary (Fig. 1). Commonly, the average of \( G_{\text{max}} \) and \( G_{\text{min}} \) is used as an estimate of the mean genus, \( \langle G \rangle \).

The 1st Betti number, \( p_1 \), (or genus, \( G \)) is a scale-dependent parameter, Eq. (1a), and for sufficiently large network sizes (or sample volumes), it becomes a linear function of the network size (or the sample volume) \([13,31,33–35]\). Instead of \( \langle G \rangle \), the specific genus, \( \langle G_v \rangle \), which is equal to the mean genus per unit volume is used as a measure of the connectivity of pore structures. After a sufficient number of serial sections have been analyzed, the specific genus is estimated from the constant slope of a plot of the mean genus vs sample volume [33].

The mean coordination number, \( \langle c_n \rangle \), of a bond-and-node pore network is a more familiar measure of the pore space connectivity, is defined as the mean number of bonds adjoining to a node and is given by

\[
\langle c_n \rangle = 2 + \frac{\langle p_1 \rangle - \langle p_0 \rangle}{n}.
\]  

Eq. (1b) is applied only to very large networks and requires reliable estimates of \( p_1 \) and \( p_0 \). A great number of large serial sections must be analyzed before a correct estimate of \( \langle c_n \rangle \) is obtained from Eq. (1b) [31]. Usually, a small volume of the sample is analyzed and only the specific genus, \( G_v \), is determined with satisfactory accuracy [35]. It must be pointed out that the specific genus is a dimensional parameter, is a measure of the connectivity density of the pore space and consequently depends not only on network connectivity but also on other geometrical characteristics of the pore structure such as the mean distance between adjacent pores [33]. Therefore, the value of \( \langle G_v \rangle \) by itself gives no information about the connectivity of a pore structure whereas no comparison between different structures can be made in terms of the values of this parameter. Nevertheless, if the value of \( \langle G_v \rangle \) is combined with other geometrical parameters of the pore space (as we will see below) then both the network skeleton is automatically quantified and useful network properties, such as the distribution of coordination number, are obtained.

### 2.2. Pore network model

The pore space is modeled as a three-dimensional network of “spherical” chambers interconnected through long “cylindrical” throats (primary network, Fig. 2) with roughness features superposed on the free surface of chambers and throats (fractal network). The chamber-diameter distribution (CSD), the throat-diameter distribution (TSD), and the primary porosity, \( \varepsilon_p \), are used as input parameters for the construction of the primary network, whereas the pore-wall roughness is modeled as a fractal surface (as it is described below) of a given fractal porosity \( \varepsilon_f \). Initially, the skeleton of the network is taken to be a regular cubic lattice, and so each chamber is connected to six neighbors through six throats (coordination number, \( c_n = 6 \)). Then, throats are removed according to the TSD and by retaining the accessibility of each chamber to the boundary throats. This procedure is continued until the specific genus \( \langle G_v \rangle \) (and hence the connectivity) of the pore network matches that of the prototype porous medium.

The assignment of sizes to the nodes and bonds of network is made according to the CSD and TSD, respectively. This procedure can be done completely at random so that no correlation exists among the sizes of chambers and those of neighboring throats (uncorrelated network). On the other hand, the assignment of sizes can be done in such a way that a c–t or a c–c and c–c correlated network is obtained [50]. Two input parameters are used in the procedure of constructing correlated networks [50]: (1) the “voting” exponent, \( n_v \), that takes the values \(-1 \) (negative c–t correlation), 0 (no c–t correlation) and \(+1 \) (positive c–t correlation) and (2) the fraction of “seed” chambers, \( a_s \), that ranges from 0 to 1.

![Fig. 2. Chamber-and-throat network model.](image-url)
and the smaller its value the stronger the c–c correlations. After the construction of a correlated pore network has been completed, the statistical correlation coefficients $\rho_{c-t}$ and $\rho_{c-c}$ of the chamber sizes with the mean sizes of adjoining throats and the mean sizes of neighboring chambers are respectively calculated. These coefficients are used as measures of the spatial correlations between the sizes of throats and those of their adjacent chambers and between the sizes of neighboring chambers, respectively.

### 2.3. Fractal roughness model

In the past, experimental and theoretical analyses revealed that pore cusps and roughness features were mainly intruded by mercury over the high-pressure region [10,18,52,58]. The fractal roughness model developed in [52] is further treated here to represent the irregular morphology of throats and chambers. The roughness features are right triangular prisms for the throats and right circular cones for the chambers of the primary network (Fig. 3). With regard to the roughness model described in Ref. [52], some modifications are made here: (a) the number of layers of roughness features extends to infinity (fractal structure of infinite specific surface area), (b) the parameters required for the determination of the roughness of such a network are the characteristic number of features per linear dimension of the previous layer, $n_r$, and the surface fractal dimension, $D_s$. The angle of sharpness is different for throats, $\omega_t$, and chambers, $\omega_c$, and is so adjusted that the fractal dimension of throats, $D_{st}$, matches that of chambers, $D_{sc}$, namely

\[ D_t = D_{st} = D_{sc}. \tag{2a} \]

where

\[ D_{st} = \frac{\ln (n_t^2 \sin \omega_t)}{\ln (n_r \sin \omega_t)}, \tag{2b} \]

\[ D_{sc} = \frac{2 \ln (n_t)}{\ln (2n_r \sqrt{\tan \omega_c / \omega_t})}. \tag{2c} \]

### 2.4. Calculation of absolute permeability

The absolute permeability of chamber-and-throat networks is calculated by analogy to the solution of electric circuits [11,18]. The pressure, the hydraulic conductance and the volumetric flow rate are equivalent to the potential, the electrical conductance and the current flow. Kirchoff’s rules formulate that the sum of the voltages is zero for every closed loop of conductors and that the algebraic sum of the currents flowing into each node is also zero. From the application of these rules to the pore network, a system of coupled linear equations for the potential at each node is obtained. This system is solved using an iterative Gauss–Seidel method. Substituting the volumetric flow rate at the inlet of network and the pressure drop along it in Darcy’s law, the absolute permeability is obtained. The fractal roughness features of throats are included in the calculation of hydraulic conductances as cylindrical tubes of equivalent cross-section area, whereas the roughness features of chambers are considered as dead-end pores and are ignored.

### 3. Serial sectioning analysis of porecasts

The experimental procedure of serial tomography as applied to a porous sample of a sedimentary rock consists of the following stages [59]:

(a) **Construction of double porecasts.** The porous sample is evacuated and is impregnated with heated liquid Wood’s metal at high-temperature ($T = 85–95^\circ$C), by applying a sufficiently high-pressure ($P = 100–150$ atm) for a period of 2–4 h. Then, the system is cooled at room temperature so that Wood’s metal is solidified. The host rock is dissolved with hydrofluoric acid and the pore cast is impregnated with the epoxy-resin ERL-4206 [47] colored with Oracet Red (MERCK). The whole system is heated to 60–70°C and
is kept at this temperature for 8–12 h, until polymerization and hardening of the resin is completed.

(b) Production of serial sections. A small piece of the porecast is sliced and is glued on a microscope glass slide. The production of polished successive sections is carried out by grinding and polishing the surface of the porecast, with a Minimet Polisher/Grinder (BUEHLER). The amount of material, that is removed at each step, is properly adjusted by regulating the speed, load and operation time of the equipment.

(c) Image acquisition. Each new polished surface of the sample is placed under an optical microscope, its image is taken with a videocamera, and is recorded in a videotape for further analysis (Fig. 4(a) and (b)).

(d) Image digitization and data storage. The video-recorded images (dimensions: 1.65 mm × 1.24 mm, Fig. 4(a) and (b)) are sent to an image analysis card (IMAGING TECHNOLOGY) which is installed in the host computer. Only the central region (dimensions: 1.08 mm × 1.04 mm, Fig. 4(c) and (d)) of the primary images is digitized. The digitization is performed automatically by a software package which uses as parameters the length of resolution of the picture (number of pixels/area) and the breakthrough gray-level between Wood’s metal and resin.

For the determination of the topological and geometrical properties of porous media, the algorithm GETPO has been developed [33] which reconstructs the three-dimensional pore network from data of two-dimensional pore features of serial sections. Primarily, the algorithm is used for the determination of the genus. In addition to the genus, the algorithm GETPO reconstructs a chamber-and-throat network that has the same topology with the actual pore network and approximates its geometry. For our purposes, the algorithm GETPO is used mainly for the determination of the mean specific genus, $G_V$, and the chamber diameter distribution, CSD.

The results of the application of the algorithm GETPO to data of 44 serial sections of a double porecast of an outcrop Grey-Vosgues sandstone (sample GV-1, Fig. 4) are given in Table 1. Using the Marquardt parameter estimation method [5], the chamber diameter distribution (CSD) and the throat diameter distribution (TSD) were fitted with bimodal distribution functions of the form
Table 1
Topological and geometrical properties of the reconstructed pore space (sample: GV-1)

<table>
<thead>
<tr>
<th>No</th>
<th>Property</th>
<th>Parameter values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Specific genus</td>
<td>( G_n = 2.9 \times 10^{-6} \text{µm}^3 )</td>
</tr>
<tr>
<td>2</td>
<td>Chamber diameter distribution (mean value, standard deviation)</td>
<td>Bimodal distribution function ( f_1(D) : (D_1) = 29.1 \mu m, \sigma_1 = 28.5 \mu m ) Component log-normal distribution functions ( f_1(D) : (D_3) = 22.0 \mu m, \sigma_3 = 10.0 \mu m ) ( f_2(D) : (D_2) = 43.5 \mu m, \sigma_2 = 44.2 \mu m ) Contribution fraction: ( c_i = 0.33 )</td>
</tr>
<tr>
<td>3</td>
<td>Throat diameter distribution (mean value, standard deviation)</td>
<td>Bimodal distribution function ( f_3(D) : (D_3) = 18.4 \mu m, \sigma_3 = 11.3 \mu m ) Component log-normal distribution functions ( f_1(D) : (D_3) = 15.3 \mu m, \sigma_1 = 4.6 \mu m ) ( f_2(D) : (D_3) = 23.3 \mu m, \sigma_2 = 16.1 \mu m ) Contribution fraction: ( c_i = 0.62 )</td>
</tr>
</tbody>
</table>

\[ f_c(D) = c_1 f_{c1}(D) + (1 - c_1) f_{c2}(D), \]

\[ f_t(D) = c_t f_{t1}(D) + (1 - c_t) f_{t2}(D), \]

respectively, where \( c_1 (c_t) \) and \( 1 - c_1 (1 - c_t) \) are the contribution fractions of the log-normal component distribution functions \( f_{c1} \) and \( f_{c2} \) (\( f_{t1} \) and \( f_{t2} \)) to the total distribution function \( f_c \) (\( f_t \)) (Table 1).

In general, every method that determines all geometrical properties of the pore space solely from three-dimensional reconstructed structures has some shortcomings, especially with reference to the less macroporous materials [33]. Specifically, throats of size smaller than the lowest limit of resolution (which is determined by the microscope magnification) are not measured or are assigned to larger sizes because they are either completely or partly “invisible”. Also, some very small throats may not be impregnated by Wood’s metal and therefore they are not seen at any magnification. In addition, short throats intervening between serial sections are not seen and are identified as parts of chambers. Therefore, the TSD obtained from serial sectioning analysis is expected to be overestimated with respect to the “actual” one and the combination of serial tomography with mercury porosimetry is necessary for the determination of the “actual” throat size distribution.

4. Analytic description of mercury porosimetry curves

4.1. Basic equations

The comparison of experimental with simulated mercury porosimetry results can highly be simplified by using parametric analytic functions to describe the mercury intrusion and retraction curves. Experimental analyses [14,15,40] and pore network simulations [18,21,36,43,49] have shown that most mercury porosimetry curves exhibit sigmoidal shape. In addition, each curve is subject to the limitation that mercury saturation goes from 0 to 1, for intrusion and from its residual value \( S_0 \) to 1, for retraction, as the capillary pressure changes from very low to very high values. All aforementioned characteristics of mercury porosimetry curves are embedded into the following 2-parameter (2-P) analytic functions.

(a) Mercury intrusion curves

\[ S = \frac{(1 + a_t) e^{-b_t/P}}{1 + a_t e^{-b_t/P}}, \quad b_t > 0, \]

\[ S = \frac{(1 + a_t)}{1 + a_t e^{-b_t/P}}, \quad b_t < 0, \]

(b) Mercury retraction curves

\[ S = \frac{S_0 + (1 + a_R - S_0) e^{-b_R/P}}{1 + a_R e^{-b_R/P}}, \quad b_R > 0, \]

\[ S = \frac{(1 + a_R - S_0) + S_0 e^{-b_R/P}}{a_R + e^{-b_R/P}}, \quad b_R < 0. \]

The functional form of the curves changes with the sign of parameters \( b_t, b_R \), Eqs. (4a), (4b), (5a), (5b) in order to keep its consistency with the aforementioned limitations of mercury porosimetry curves. The median pressures \( P_1, P_R \) specify the pressure range of intrusion and retraction curves whereas the mean slopes \( s_1, s_R \) specify the width of the corresponding curves. These parameters are defined at saturation values \( S = 1/2 \) for mercury intrusion and \( S = (1 + S_0)/2 \) for mercury retraction, respectively, and are given below.

(a) Characteristic parameters of mercury intrusion curves

\[ P_1 = \frac{b_t}{\ln(a_t + 2)}, \quad b_t > 0, \]

\[ P_1 = \frac{b_t}{\ln(a_t/(2a_t + 1))}, \quad b_t < 0, \]
functions makes easier and more efficient any comparison between experimental curves of different porous rocks, or between experimental curves and simulated results.

In mercury porosimetry, the breakthrough pressure [15] is defined as the minimum pressure at which mercury forms a connected pathway along the porous sample for a first (during intrusion) or last (during retraction) time. In terms of percolation theory, the breakthrough pressure is related with the percolation threshold of the pore network [45] and depends on geometrical and topological properties of the pore structure [10,15,19,44,45,54]. It has been found [23,40] that the measured breakthrough pressure corresponds graphically to the inflection point on a mercury intrusion plot (this is where the mercury intrusion curve becomes convex downward).

The breakthrough pressures of intrusion, \( P_{IB} \), and retraction, \( P_{RB} \), are defined at the inflection points of the mercury intrusion and retraction curves, respectively. These pressures are determined by setting the second derivative of each analytic function of Eqs. (4a), (4b), and (5a), (5b) equal to zero. Finally, there are obtained

\[
\begin{align*}
S_1 &= \frac{(a_1 + 2)\ln^2(a_1 + 2)}{4b_1(a_1 + 1)}, \quad b_1 > 0, \\
S_1 &= -\frac{(2a_1 + 1)\ln^2(a_1/(2a_1 + 1))}{4b_1(a_1 + 1)}, \quad b_1 < 0.
\end{align*}
\]

(b) Characteristic parameters of mercury retraction curves

\[
\begin{align*}
P_R &= \frac{b_R}{\ln(a_R + 2)}, \quad b_R > 0, \\
P_R &= -\frac{b_R}{\ln(a_R + 2)}, \quad b_R < 0, \\
s_R &= \frac{(1 - S_0)(a_R + 2)\ln^2(a_R + 2)}{4b_R(a_R + 1)}, \quad b_R > 0, \\
s_R &= -\frac{(1 - S_0)(a_R + 2)\ln^2(a_R + 2)}{4b_R(a_R + 1)}, \quad b_R < 0.
\end{align*}
\]

The parameter values \((a_i,b_i)\) and \((a_R,b_R)\) of intrusion and retraction curves are estimated separately for each sample using a properly adjusted unstrained Marquardt method of non-linear least squares [5]. The experimental mercury porosimetry curves of a carbonate and a sandstone are compared to the corresponding ones given by the analytic fitting functions in Fig. 5(a) and (b). Although the 2-P functions fit satisfactorily to curves of narrow pressure range (carbonate C-4, Fig. 5(a)) they are unable to fit curves of a wide pressure range (sandstone BS-1, Fig. 5(b)). In order to improve the fitting to mercury porosimetry curves, 5-parameter (5-P) functions resulting from the linear combination of two 2-P functions are used.

(a) Intrusion curve

\[
S = c_iS_1(P; a_{i1}, b_{i1}) + (1 - c_i)S_2(P; a_{i2}, b_{i2}),
\]

\[
S_j(P; a_{ij}, b_{ij}) = \frac{(1 + a_{ij})e^{b_{ij}/P}}{1 + a_{ij}e^{b_{ij}/P}}, \quad b_{ij} > 0, \quad j = 1, 2.
\]

(b) Retraction curve

\[
S = c_RS_1(P; a_R, b_{R1}) + (1 - c_R)S_2(P; a_R, b_{R2})
\]

\[
S_j(P; a_{Rj}, b_{Rj}) = \frac{S_0 + (1 + a_{Rj})e^{-b_{Rj}/P}}{1 + a_{Rj}e^{-b_{Rj}/P}}, \quad b_{Rj} > 0, \quad j = 1, 2.
\]

The median pressure and mean slope of each component curve are given by Eqs. (6a), (6b), (7a), (7b), (8a), (8b), (9a), (9b). The fitting of the curves of sandstone BS-1 is improved substantially with the 5-P functions (Fig. 5(b)). The description of mercury porosimetry curves in terms of the parameters of the specific analytic functions makes easier and more efficient any comparison between experimental curves of different porous rocks, or between experimental curves and simulated results.

In mercury porosimetry, the breakthrough pressure [15] is defined as the minimum pressure at which mercury forms a connected pathway along the porous sample for a first (during intrusion) or last (during retraction) time. In terms of percolation theory, the breakthrough pressure is related with the percolation threshold of the pore network [45] and depends on geometrical and topological properties of the pore structure [10,15,19,44,45,54]. It has been found [23,40] that the measured breakthrough pressure corresponds graphically to the inflection point on a mercury intrusion plot (this is where the mercury intrusion curve becomes convex downward).

The breakthrough pressures of intrusion, \( P_{IB} \), and retraction, \( P_{RB} \), are defined at the inflection points of the mercury intrusion and retraction curves, respectively. These pressures are determined by setting the second derivative of each analytic function of Eqs. (4a), (4b), and (5a), (5b) equal to zero. Finally, there are obtained

\[
b_1 - 2P_{IB} - (2P_{IB} + b_1)a_1e^{-b_1/P} = 0, \quad (12a)
\]

\[
b_R - 2P_{RB} - (2P_{RB} + b_R)a_Re^{-b_R/P} = 0. \quad (12b)
\]

When the mercury intrusion/retraction curves are fitted with 5-P functions, then \( P_{IB} \) and \( P_{RB} \) are regarded as the inflection points of the low-pressure 2-P component functions. Such an approach is based on the realistic assumption that the low-pressure component function reflects the filling or the emptying of the primary pore network while the high-pressure component function reflects the filling or the emptying of the pore wall roughness. Note that the parameters \( P_{IB} \) and \( P_{RB} \) are not strictly equal but are expected to be comparable to the real capillary pressures at which mercury forms a network spanning cluster for a first and a last time, respectively. These parameters are additional quantitative measures of comparison between experimental and simulated mercury porosimetry curves.

4.2 Application to simulated curves

Details about the simulator of mercury intrusion/retraction in chamber-and-throat networks are reported in Refs. [49–52]. 2-P functions were fitted to existing simulated curves of smooth-wall pore networks [49–51] and the results are shown in Table 2(a)–(c). By using a cubic primary pore network with log normal CSD \((D_c) = 40 \mu \text{m}, \sigma_c = 15 \mu \text{m})\) and TSD \((D_s) = 10 \mu \text{m}, \sigma_s = 5 \mu \text{m})\), simulated mercury intrusion/retraction curves were produced as functions of the fractal roughness properties \(D_s\) and \(c_i/c_{i0}\). 5-P functions were
fitted to these curves and the results are shown in Table 2(d). Based on the results of Table 2(a)–(d), a parameter covariance matrix was constructed (Table 3), where the variation of each structural parameter of the pore network was correlated with the variation of the parameters of the corresponding fitting functions. The covariance matrix of Table 3 can be used as a guide within a scheme of iterative parameter estimation, as we will see below. The 5-P functions are more suitable than the 2-P functions for the fitting of almost all mercury porosimetry curves without excluding the necessity of using 8-P or higher parameter order functions to fit exceptionally complex curves. However, each of these functions is nothing but the linear combination of 2-P functions. Hence, the use of 2-P functions is aimed at clarifying the physical meaning of the characteristic parameters of the fitting functions and understanding the correlations of these parameters with the actual properties of the pore structure (Tables 2(a)–(d) and 3). Such correlations are difficult to be deconvoluted directly from 5-P functions. In the following, 5-P functions are used to fit experimental and theoretical mercury intrusion/retraction curves.

5. Method of characterization of pore structures

The microstructural characterization of a sample of a given rock, in terms of a chamber-and-throat network, is performed with an algorithm that combines data of...
serial tomography with experimental mercury porosimetry curves and simulations of mercury intrusion/retraction in pore networks. The iterative procedure used to estimate the pore structure parameters is illustrated in Fig. 6. The following steps are included in this scheme of analysis.

(a) The porosity of the sample is measured with imbibition method [15].

(b) The absolute permeability of the sample is measured with gas permeametry [15].

(c) The mean specific genus \( G_v \) and the chamber-diameter distribution CSD are obtained from serial sectioning analysis of a double porecast of the porous sample.

(d) The mercury porosimetry curves of the sample are measured and then are fitted with 5-P analytic functions.

### Table 2
Parameters of the fitting functions of simulated mercury intrusion/retraction curves

<table>
<thead>
<tr>
<th>((D_t)_{(\mu m)})</th>
<th>(\sigma_t (\mu m))</th>
<th>(P_I (MPa))</th>
<th>(s_I (MPa^{-1}))</th>
<th>(P_R (MPa))</th>
<th>(s_R (MPa^{-1}))</th>
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### Table 3
Covariance matrix

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<td>0.775</td>
<td>0.1340</td>
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<td>0.655</td>
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<td>0.725</td>
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</table>

Events of the fractal roughness properties

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<th>(\epsilon_t/l_t)</th>
<th>(\epsilon_1)</th>
<th>(P_{I1})</th>
<th>(s_{I1})</th>
<th>(P_{I2})</th>
<th>(s_{I2})</th>
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</thead>
<tbody>
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<td>0.775</td>
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<td>31.871</td>
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<tr>
<td>2.35</td>
<td>8</td>
<td>0.412</td>
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<td>2.35</td>
<td>40</td>
<td>0.153</td>
<td>0.725</td>
<td>0.1331</td>
<td>36.518</td>
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</tbody>
</table>
(e) The throat diameter distribution TSD and the primary porosity are estimated from the experimental mercury intrusion curve. A first estimate of the TSD is obtained by differentiating the mercury intrusion curve according to the conventional method of analysis that is based on the tube bundle model of the pore structure [14].

(f) A theoretical chamber-and-throat network of finite dimensions is constructed (Fig. 7). The input values of certain parameters (0) are slightly different from their output values (2) because the construction of the pore network is made under some limitations due to the requirements concerning the realistic representation of the pore space:

1. No intersection of adjacent chambers is allowed.
2. Throats adjoining to a chamber are not allowed to intersect outside the chamber.
3. Each chamber remains accessible to the network boundaries through at least one uninterrupted continuous pathway of throats and chambers.
4. Throats are removed randomly and according to the estimated TSD until the specific genus of the theoretical pore network matches that of the porous sample.

Obviously, the differences between input (0) and output (2) parameter values are expected to increase as the overlapping between the TSD and the CSD increases or the degree of the spatial pore size correlations (arrangement of small or large sizes in adjacent positions) increases. The distribution of the coordination number is calculated after the construction of the irregular network has been completed. The fractal properties of the pore network (Fig. 7) are so selected that the total porosity of the simulated network matches that of the porous sample.

(g) Mercury intrusion and retraction in the theoretical chamber-and-throat network are simulated [49] and the absolute permeability of the pore network is calculated.

(h) The simulated mercury intrusion and retraction curves are fitted with 5-P analytic functions.

(i) The values of the characteristic parameters of the analytic functions of simulated mercury intrusion/retraction curves are compared with the corresponding ones of the experimental curves. In addition, the

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**Fig. 6.** Method of characterization of a pore structure in terms of chamber-and-throat network models.
The experimental value of absolute permeability is compared with its theoretical value. If significant differences are found, the values of the pore network parameters alter. The procedure is repeated until the experimental mercury porosimetry curves and the absolute permeability are predicted satisfactorily. The following effects of pore network parameters on mercury porosimetry curves (Table 2(a)–(d)) are taken into account to estimate the new parameter values.

1. As the mean value of the TSD increases, the steepest part of the intrusion curve (which corresponds to the filling and emptying of the greatest fraction of the pore network and takes place over the low-pressure region) moves to lower pressures whereas the width of the intrusion and retraction curves decreases (Tables 2(a) and 3).

2. As the TSD widens, both mercury intrusion and retraction curves move toward lower pressures, the width of intrusion curve increases and the width of retraction curve decreases (Tables 2(a) and 3).

3. As the mean coordination number decreases, the intrusion curve moves to higher pressure range, its width increases, the loop of hysteresis between the intrusion and retraction curves widens and the residual mercury saturation increases (Tables 2(b) and 3).

4. As the degree of the spatial pore size correlations increases, the intrusion curve widens whereas the mercury retraction curve moves to lower pressure range and its width decreases (Tables 2(c) and 3).

5. When the fractal dimension increases, the intrusion curve widens toward high pressures whereas the retraction curve widens and moves to higher pressures as well (Tables 2(d) and 3).

6. The specific genus of the simulated network is very sensitive to the length of periodicity of the lattice. The primary porosity $\varepsilon_i$ influences the length of periodicity of the pore network and hence it has a pronounced effect on the mean value of coordination number that is reached when the specific genus of the network matches its experimental value.

7. The absolute permeability of the pore network [11] is affected mainly by the TSD and the pore network connectivity (namely, the coordination number distribution).

6. Results and discussion

The above methodology was applied to the estimation of the parameter values of a sample (GV-1) of an outcrop Grey-Vosges sandstone.

(a) The porosity of the sample was measured and found to be $\varepsilon_i = 0.18$.

(b) The gas permeability of the sample was measured and found to be $k = 110$ md.
(c) The specific genus \(G_v\) and the chamber diameter distribution, CSD were determined by using serial sectioning analysis of a double porecast (Table 1).

(d) The experimental mercury porosimetry curves were fitted with 5-P analytic functions and the optimum parameter values were determined (Fig. 8). The mercury intrusion curve was decomposed to two component curves extending over the low- and high-pressure range, respectively (Fig. 8).

(e) By assuming that the coefficient \(c_1\) (Fig. 8) is roughly comparable to the ratio of the primary to the total porosity \(\varepsilon_p/\varepsilon_t \approx 0.55\), the low-pressure component of intrusion curve was differentiated according to the conventional method of analysis and a log normal TSD with parameter values \(D_s = 12.2\ \mu m, \sigma_s = 2.45\ \mu m\) was obtained. Theoretical simulation has shown that the actual TSD of an uncorrelated network is usually wider than that obtained with differentiation because of “shadowing” network effects [49]. A log normal TSD (0) with parameter values \(D_s = 12.5\ \mu m, \sigma_s = 4.0\ \mu m\) and a primary porosity \(\varepsilon_p = 0.11\) was selected.

(f) When the construction of the primary chamber-and-throat network was completed the output log normal TSD (2) as well as any other network parameter were calculated (NET1, Tables 4 and 5). The choice of the fractal properties \(D_s = 2.45, n_r = 12\) was made so that the size range of roughness features be sufficiently wide because the slope of the high-pressure component \(s_{12}\) of intrusion curve is quite low (GV-1, Table 6).

(g) Mercury intrusion in and retraction from the network were simulated and the theoretical absolute permeability was determined (NET1, Table 4).

(h) The optimum values of the characteristic parameters of the analytic fitting functions of the simulated intrusion/retraction curves were determined (NET1, Table 6).

(i) The theoretical results were compared with the experimental data and new estimates of the parameter values were made based on data of Table 3. The TSD was kept nearly constant while the mean coordination number was decreased by adjusting the value of the primary porosity \(\varepsilon_t\). The other parameters were changed accordingly (NET2, Tables 4 and 5). In this manner, the agreement of theoretical with experimental results was improved substantially with respect to both mercury porosimetry curves (NET2, Table 6) and absolute permeability (NET2, Table 4). Consecutive iterations revealed that simulations on pore networks with unimodal TSDs were unable to predict simultaneously the capillary behavior (Fig. 9(a)) and permeability of the porous sample (Tables 4 and 6). For this reason, simulations on pore networks with bimodal TSDs, Eq. (3b), were attempted (POR1–POR2, Tables 4 and 5). Although with the use of bimodal TSDs the predictability of the experimental data was improved (Fig. 9(b), Tables 4 and 6), some important characteristics of the capillary behaviour of the porous sample GV-1, such as the relatively low \(c_1\) value (which means that the contribution fraction of the low-pressure component curve on the overall intrusion curve is almost the same with the corresponding one of the high-pressure component curve) were not well-predicted by using uncorrelated networks and bimodal TSDs (Table 6). With the use of strongly c–c and c–t correlated chamber-and-throat networks and bimodal TSDs (CP1–CP3, Tables 4 and 5) the agreement of simulated results with the experimental data became satisfactory (Fig. 10, Tables 4 and 6).

The breakthrough pressures and permeability of the network CP3 are very close to the corresponding ones of the sample GV-1 (Fig. 10(b)). The parameters of the analytic fitting functions of mercury intrusion curve of the CP3 network are also very close to the corresponding ones of GV-1 sample but there is a discrepancy with
The relatively high slope of the last part of the mercury retraction curve increases the sigmoidity of porosimetry data but by using the tube bundle finite-size effects are eliminated and the mean slope of the retraction curve changes.

Table 4

Parameters of the theoretical chamber-and-throat networks used in simulations

<table>
<thead>
<tr>
<th>NET</th>
<th>( \langle D_h \rangle ) (μm)</th>
<th>( \sigma_h ) (μm)</th>
<th>( \langle D_t \rangle ) (μm)</th>
<th>( \sigma_t ) (μm)</th>
<th>( \langle s_h \rangle )</th>
<th>( G_V \times 10^8 ) (μm(^{-1}))</th>
<th>( D_S )</th>
<th>( n_i/l_i )</th>
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<th>( \rho_{e-t} )</th>
<th>( k ) (md)</th>
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Table 5

Parameters of the component distribution functions of the CSD and TSD

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<th>( \sigma_{h,i} ) (μm)</th>
<th>( \langle D_{t,i} \rangle ) (μm)</th>
<th>( \sigma_{t,i} ) (μm)</th>
<th>( c_i )</th>
<th>( \langle D_{h,i} \rangle ) (μm)</th>
<th>( \sigma_{h,i} ) (μm)</th>
<th>( \langle D_{t,i} \rangle ) (μm)</th>
<th>( \sigma_{t,i} ) (μm)</th>
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<td>–</td>
</tr>
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<td>40.98</td>
<td>0.59</td>
<td>13.85</td>
<td>1.8</td>
<td>3.07</td>
<td>11.44</td>
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Table 6

Parameters of the analytic fitting functions of mercury intrusion/retraction curves

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<th>Pore net</th>
<th>( c_i )</th>
<th>( P_{h1} ) (MPa)</th>
<th>( s_{h1} ) (MPa (^{-1}))</th>
<th>( P_{h2} ) (MPa)</th>
<th>( s_{h2} ) (MPa (^{-1}))</th>
<th>( c_R )</th>
<th>( P_{r1} ) (MPa)</th>
<th>( s_{r1} ) (MPa (^{-1}))</th>
<th>( P_{r2} ) (MPa)</th>
<th>( s_{r2} ) (MPa (^{-1}))</th>
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<tbody>
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<td>0.243</td>
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<td>0.0570</td>
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<td>2.11</td>
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<td>1.873</td>
<td>0.925</td>
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<td>0.0018</td>
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<td>0.2727</td>
<td>0.630</td>
<td>0.0434</td>
<td>11.305</td>
<td>1.986</td>
<td>0.0557</td>
</tr>
<tr>
<td>CP3</td>
<td>0.63</td>
<td>0.1187</td>
<td>20.76</td>
<td>1.017</td>
<td>0.246</td>
<td>0.675</td>
<td>0.0382</td>
<td>13.655</td>
<td>2.01</td>
<td>0.0635</td>
</tr>
</tbody>
</table>

With respect to the mean slope of the low-pressure component function of the mercury retraction curve, \( s_{h1} \) (Table 6), the relatively high slope of \( s_{h1} \) of the CP1–CP3 networks (Table 6) is due to the fact that the boundary effects on the last part of mercury retraction curve increase significantly in strongly correlated pore networks [50]. Simulations in pore networks of dimensions much larger than those used here (20×20×20) are needed so that finite-size effects are eliminated and the mean slope of the low-pressure component function of the retraction curve is reduced.

In Fig. 11, the TSDs of the strongly correlated simulated networks (TSD1–TSD3) are compared with the TSDs obtained from the serial sectioning analysis (TSD4, Table 1) and the conventional method of analysis of porosimetry data but by using the tube bundle model (TSD5). The serial sectioning analysis (TSD4, Fig. 11) is unable to account for throats of small sizes (smallest pore feature traced ~2 μm) and hence the prediction of the flow properties of the reconstructed three-dimensional pore space becomes questionable [24].

On the other hand, new techniques have appeared, where the three-dimensional pore structure is reconstructed from only one section with the aid of an autocorrelation function. These techniques have no limitation on the pore size range and seem very promising for the accurate determination of certain mesoscopic transport properties of homogeneous porous media [20,60]. However, these three-dimensional reconstructed structures must be combined with time-consuming computational tools, such as cellular automata [45] to simulate multiphase transport processes.
The conventional method of analysis [14] gives a “pore-size distribution” (TSD5, Fig. 11) that is comparable to the TSDs obtained with the present method (TSD1, TSD2, TSD3 – Fig. 11). However, no further information is provided about any other properties of the porous structure. For instance, the absolute permeability of a bundle of parallel capillary tubes is given by the following approximate relationship [15]

\[ k = \frac{\varepsilon_t}{96} \left( \sigma_i^2 + \langle D_i \rangle^2 \right) \]  

which yields a value \( k = 205 \text{ md} \) if the parameter values of TSD5 are used. Therefore, the conventional “pore-size distribution” is insufficient to predict correctly the mesoscopic single-phase transport properties of porous materials and hence the topological, correlational and fractal properties of the porous microstructure must be taken into account, as well. Apparently, the estimated TSDs of the correlated networks CP2 and CP3 (Fig. 11) as well as their component distribution functions (Table 5) are very close each other. This means that the TSD starts to converge to a unique bimodal distribution function after utmost three iterations. Also, both the correlation coefficients \( \rho_c-c \), \( \rho_c-t \) and the fractal properties \( D_s \), \( \varepsilon_f/\varepsilon_t \) of the CP2 and CP3 seem to converge to constant values (Table 4). The observed difference between the permeabilities of CP2 and CP3 is due to their different mean coordination number (Table 4). For any further improvement of the prediction of the capillary and flow properties of the investigated porous sample, the TSD as well as the parameters \( \rho_c-c \), \( \rho_c-t \), \( D_s \), \( \varepsilon_f/\varepsilon_t \) of the simulated networks should be kept almost unaltered and only the mean coordination number be adjusted to match the experimental data.

Fig. 9. Comparison between 5-parameter analytic fitting functions of the experimental (GV-1) and simulated mercury intrusion/retraction curves. Uncorrelated chamber-and-throat networks with: (a) unimodal and (b) bimodal TSDs.
From petrographic analyses of Grey-Vosgues, it is well-known \[16\] that a small amount of clay is present upon the grain surface but does not form any secondary pore networks inside the solid matrix. Therefore, the presence of clays may affect the fractal dimension, \(D_s\), but not the ratio \(e_t/e_c\).

The determination of the surface fractal dimension from the high-pressure characteristics of capillary pressure curves is not a new idea \[48\]. However, except for the fractal dimension, the present method estimates the fractal roughness porosity so that the values of both parameters are consistent with the values of the other pore network parameters. Furthermore, there are many other methods for the determination of the fractal properties of porous materials at small length scales as for instance, the fracture surface technique \[25\], the nitrogen adsorption \[46\], the small angle X-ray scattering \[4\], the neutron scattering \[58\], etc. The reliability of the present method with respect to the calculation of the fractal dimension values could be evaluated in comparison with corresponding values obtained from either the analysis of two-dimensional images of random sections at several magnifications or nitrogen adsorption isotherms, but this is beyond the scope of the present work.

With reference to the one-phase transport coefficients, the present methodology is self-predictive because the consistency of the experimental with the theoretical absolute permeability is included in the iterative procedure of pore structure parameter estimation (Fig. 6). Although the theoretical tools needed for the calculation of multiphase transport properties of reservoir rocks from microscopic properties of the pore structure have already been developed \[12,54\], there is currently a lack of experimental data about the relative permeability and resistivity index curves of the investigated core of Grey-Vosgues. When such data are obtained, then the existing theoretical simulators will be able to be used for the evaluation of the reliability of the present method of pore structure characterization with respect to the predictability of multiphase transport coefficients. Nevertheless, such an investigation can become the subject of a forthcoming publication.

### 7. Conclusions

A methodology was developed for the characterization of the porous structure of reservoir rocks in terms of chamber-and-throat networks. The chamber (equivalent spherical) diameter distribution and specific genus...
of the porous structure are obtained with application of a three-dimensional reconstruction algorithm [33] to serial section data of double porecasts. The throat (equivalent cylindrical) diameter distribution function, the spatial correlation coefficients of the pore sizes and the parameters of the fractal porosity of the pore-wall roughness are estimated by comparing the experimental with simulated mercury intrusion/retraction curves and the experimental with the theoretical value of the absolute permeability. The mercury intrusion/retraction curves are fitted with 5-P analytic functions and any comparison of experimental data with simulated results is made in terms of certain characteristic parameters of these functions. Application of the method to the characterization of the structure of an outcrop Grey-Vosges sandstone (sample GV-1) indicated that the simultaneous prediction of capillary (mercury intrusion/retraction curves) and flow (absolute permeability) properties is accomplished under the following assumptions: (a) the throat diameter distribution is bimodal, (b) strong c-c and c-t spatial correlations between pore sizes exist, (c) the fractal dimension is ca. 2.45 and the fractal roughness porosity is ca. 0.4 and (d) the mean coordination number of the pore network ranges from 4.4 to 4.7.

The most significant novel contributions of the present method on the characterization of the structure of reservoir rocks are summarized below:

- The comparison of experimental with simulated mercury porosimetry curves is simplified by using the characteristic parameters of analytic fitting functions.
- The computer-aided construction of irregular networks is based on the specific genus rather than on the mean coordination number.
- The fractal dimension and fractal porosity are determined simultaneously from mercury porosimetry curves in a manner that keeps their values consistent with the values of the other parameters of the pore network.
- The iterative procedure of parameter estimation is simplified by using a covariance matrix into which information concerning the effects of pore network parameters on simulated mercury porosimetry curves is embedded.
- The complete microstructural characterization of porous rocks in terms of chamber-and-throat networks provides all necessary parameter values of the pore space to simulate multiphase transport processes in such pore networks.

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References


