Client		Sample modelling report			
Report Number		FR1111002			
Issue No:	1	Issue Date:	21/09/2011	First Issue Date:	21/09/2011
Job Type		Consultancy (outside ISO 9001:2008)			

Proof of Concept: Porexpert determination of permeability of ceramic and composite sample

Prepared For:

Prepared By:

Dr. Christopher M. Gribble

Checked By:

Prof. G. Peter Matthews

Contact:

Professor G. Peter Matthews
School of Geography, Earth and Environmental Sciences
Davy 601a
University of Plymouth
Plymouth
PL4 8AA
Tel: 01752 584798
Email: pmatthews@plymouth.ac.uk

ENVIRONMENTAL & FLUID MODELLING GROUP

Introduction

We were requested to provide a brief report of the capabilities of Porexpert (which is the next generation of Pore-Cor Research Suite) in the modelling of the permeability of ceramic samples. This report should be regarded as establishing Proof of Concept of the applicability of the modelling software for predicting the permeability of ceramics from mercury porosimetry, and should not be regarded as a full scientific investigation. It uses the first trial version of Porexpert (Alpha 1), and so is also a Proof of Concept of the new software, as well as confirmation of the simulation methods which have already been validated in publications about Pore-Cor.

We were provided with two mercury porosimetry data curves measured on a Thermo Scientific Pascal 140 mercury porosimeter. This report has been based on this experimental data alone, without any further knowledge of the samples being provided. The samples are identified using the identification provided by Thermo Fisher scientific, namely 111570127303 and Spain test file

Before modelling mercury porosimetry data, we recommend that a blank mercury porosimetry run is performed to correct for compressibility of the mercury, expansion of the sample chamber and compression of the sample as explained by Gane *et al.* [1]. However, the maximum pressure of the intrusion curves sent to us was too low for compressibility effects to be significant, so such effects were ignored in this study.

Background

The software "Pore-Cor Research Suite" (www.pore-cor.com) is a suite of four programs used to investigate pore-level properties of materials. The software can be used with mercury porosimetry, water retention or porometry data. For more information about determination of pore size and permeability of filter media which was used as a calibration procedure for Pore-Cor Research Suite, see the publication by Gribble *et al.* [2].

The software Porexpert is an enhanced version of Pore-Cor, with the ability to handle unit cells larger than the fixed 10*10*10 unit cell of Pore-Cor (comprising 1000 pores and up to 3000 throats). A unit cell is a three-dimensional representation of internal void structure, with periodic boundary conditions which allow the structure to repeat, and interconnect, infinitely in every Cartesian direction. Porexpert provides more realistic simulations of permeability, as the effects of boundary conditions are reduced when using larger unit cells. Voids are represented by cubic pores connected by cylindrical throats. Although the shapes of the voids are simplistic, their sizes and interconnectivity, which are the main determinants of permeability and percolation, give a network which closely matches experimental data.

The simulated network structures are generated to reproduce as closely as possible the intrusion percolation characteristics of the samples as measured by mercury porosimetry experiments. The experimental data is interpreted using the Laplace-Washburn equation, eq [1], which relates applied pressure with pore diameter.

$$d = \frac{-4\gamma cos\theta}{P} \qquad [1]$$

where d is the diameter, γ is the interfacial tension, ϑ is the mercury contact angle and P is the applied pressure. The experimental porosimetry curve is fitted using iterative trials of pore and throat sizes, and the structure which gives the closest match of mercury intrusion characteristics is chosen. The fitting process is undertaken using an annealed simplex algorithm, which works to find the global minimum for a five dimensional surface [3].

A long standing problem in the study of porous media has been the question of how to calculate the permeability of a solid from a knowledge of the geometry of the void space within it. The absolute permeability k of a porous solid is traditionally defined in terms of Darcy's law. With reference to a cell of the solid of unit volume, this may be written, eq [2]:

$$\left(\frac{dV}{dt}\right)_{cell} = \frac{k\, A_{cell}\, \delta P_{cell}}{\mu\, l_{cell}} \qquad [2]$$

where μ is the viscosity of the fluid, $(dV/dt)_{\text{cell}}$ is the volumetric flow rate across the cell, $dP_{\text{cell}}/l_{\text{cell}}$ is the pressure gradient across the length l_{cell} of the cell, and A_{cell} is the cross-sectional area. Many attempts have been made to calculate k from primary parameters such as the diameters, lengths and positions of the pores and throats [4].

An incompressible fluid flowing through a tube takes up a parabolic velocity profile, with maximum flow rate down the centre of the tube. If the flow at the walls is assumed to be zero, integration over the velocity profile yields the Poiseuille equation:

$$\left(\frac{dV}{dt}\right)_{tube} = -\frac{\pi r_{tube}^4\, \delta P_{tube}}{8\mu\, l_{tube}} \qquad [3]$$

$(\mathrm{d}V/\mathrm{d}t)_{\text{tube}}$ is the volume flow rate, r_{tube} the radius of the tube and $\mathrm{d}P_{\text{tube}}/l_{\text{tube}}$ is the pressure gradient along the tube.

The Poiseuillian flow for each pore-throat-pore arc is calculated using parameterised Navier Stokes relationships for laminar flow in square and cylindrical tube cross sections[4], corrected for anisotropy if appropriate [5]. From this point on, the permeability of the whole unit cell is calculated in a somewhat unorthodox manner. Instead of calculating the pressures at each node explicitly, as for example in the resistor network calculations of Payatakes and co-workers, we calculate the total flow capacity of the network. Since no flow is allowed against the overall pressure gradient, there is an implicit, but not explicit pressure gradient.

We assume that Poiseuillian flow occurs across the whole cell in the *-z* direction, i.e. from the top to the bottom face of the unit cell. Then

$$\left(\frac{dV}{dt}\right)_{cell;-z} = -\frac{\pi}{8\mu}\Omega\left(r_{tubes;-z}^4\right)_{cell}\frac{\delta P_{cell}}{l_{cell}} \qquad [4]$$

Ω is an averaging operator over the whole unit cell operating on the flow capacities of the individual radii $r_{\text{tube;z}}$ of all tubes lying parallel to the z axis. Ω is calculated by means of the 'Dinic' network analysis algorithm. This assumes trickle flow through the network, i.e. individual unbroken streams

of flowing fluid, several of which can flow through the same void. Although there is no explicit pressure gradient in the cell, an implicit gradient is applied by preventing the fluid flowing in the upwards (+*z*) direction.

Ω is parameterised such that eq. [4] is satisfied, and generates a term which is related to the effective Poiseuillian capacity of the cell for flow in the -*z* direction. Since at this stage of the calculation, all the tube lengths $l_{tube;z}$ are identical and $l_{tube;z} = l_{cell}/b$, where *b* is the number of tubes in the *z* direction in the unit cell (in this case 10, 15 or 20), we can include these lengths in the averaging function, so that

$$\left(\frac{dV}{dt}\right)_{cell;-z} = -\frac{\pi}{8\mu}\Omega\left(\frac{r^4_{tubes;z}}{\beta l_{tubes;z}}\right)_{cell}\delta P = -\frac{\pi}{8\mu}\Omega\left(\frac{r^4_{tubes;z}}{l_{tubes;z}}\right)_{cell}\frac{\delta P}{\beta} \qquad [5]$$

By considering tubes in the *x* and *y* directions as well, and comparing with the Darcy equation, eqn. [2], it follows that

$$k = \frac{\pi}{8\beta}\Omega\left(\frac{r^4_{tube}}{l_{tube}}\right)_{cell}\frac{l_{cell}}{A_{cell}} \qquad [6]$$

Once this equation is corrected for slip flow [4], a permeability may be calculated [6]. The publication by Gribble *et al.* , mentioned above, illustrates this approach for the simulation of the absolute permeabilities of filters [2].

Modelling of the experimental data

The Porexpert software was used to generate three different sizes of unit cell and then determine the network flow capacity, and hence absolute permeability. The two experimental curves in Figure 1 were used as the bases of the simulations. With increasing applied pressure of mercury, corresponding to decreasing size of void feature on the horizontal axis via eq [1], the curves asymptote towards the porosities of the samples.

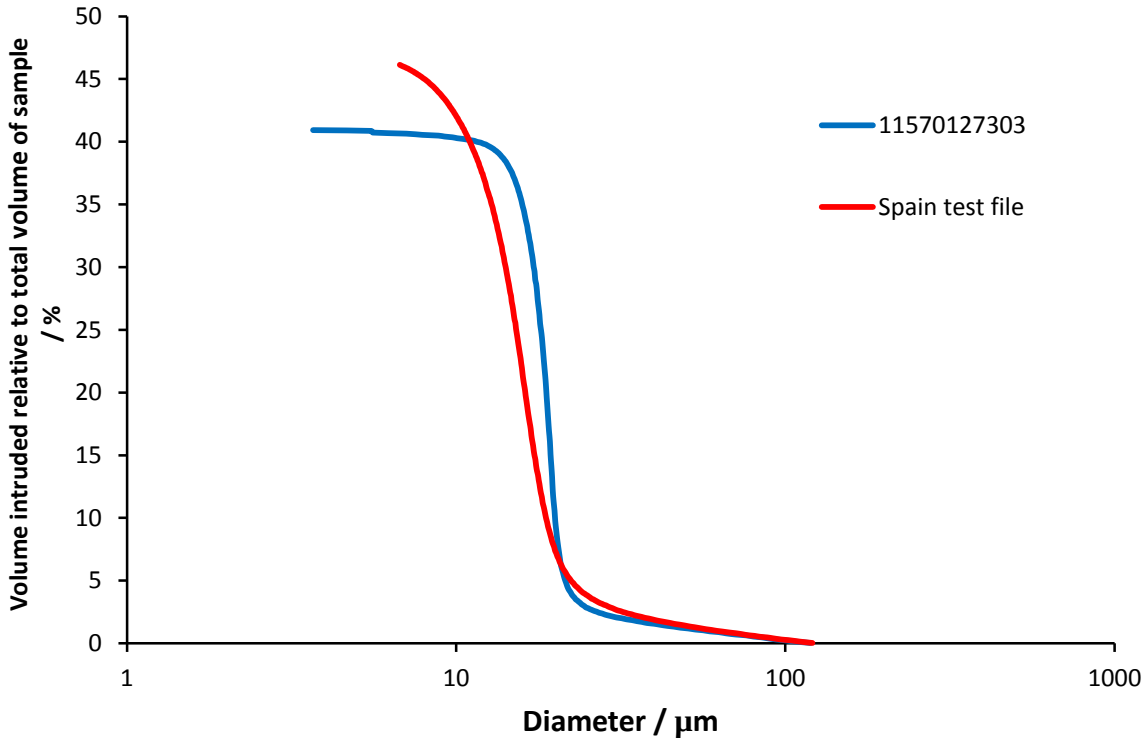

Figure 1 Graph showing the differences between the two experimental curves.

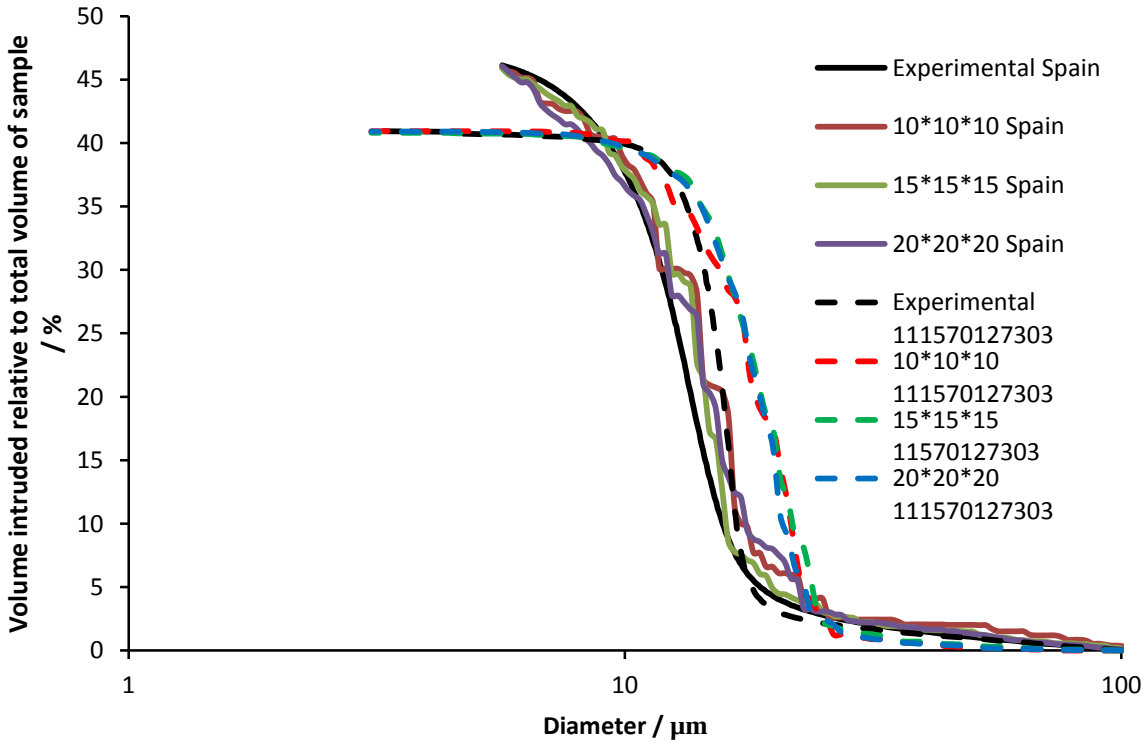

Figure 2 Comparison of experimental and simulated intrusion curves for both experimental systems with different unit cell sizes.

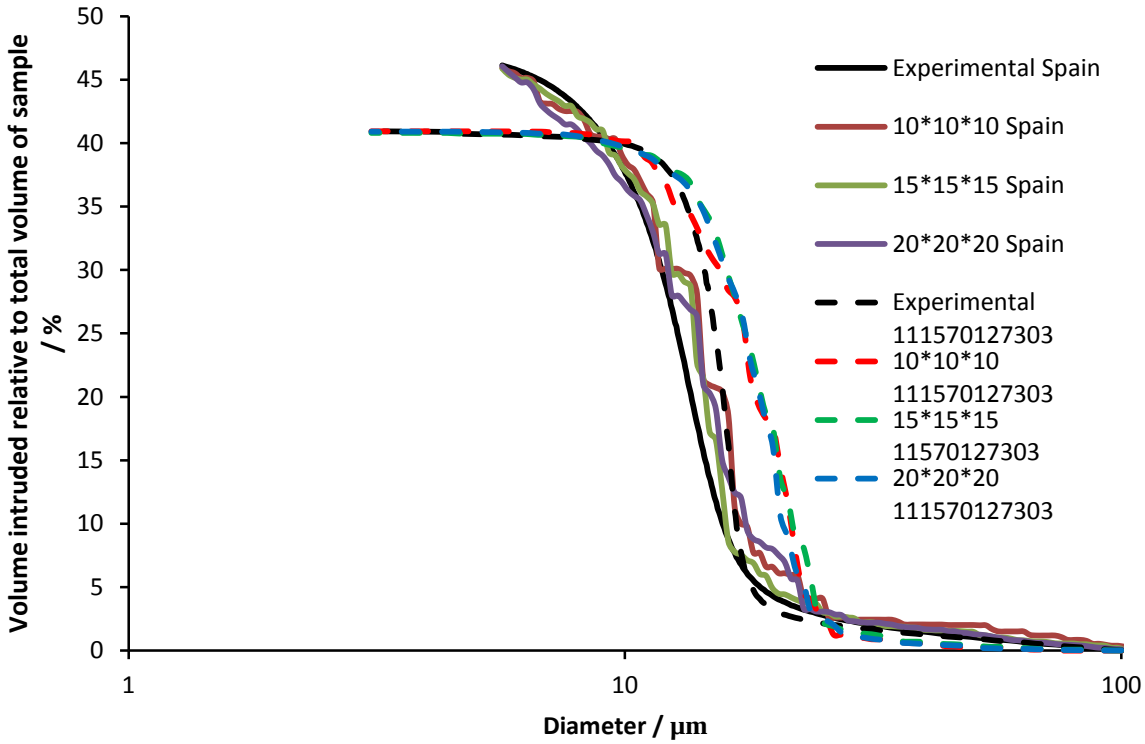

Figure 2 above shows the fits between the experimental and simulated intrusion curves. The average deviation, the maximum deviation of the three simulated curves, over the whole range of the 'Experimental Spain' curve was 1.86%, where 100% represents the full range of volume intruded and the full range of diameter (or pressure) on a logarithmic scale. This fit is currently equally weighted by experimental points at zero and near-maximum intrusion, relative to what should be the more important measurements at the point of inflexion. This presents a problem, as explained in the Conclusions below, and the weighting will be modified in a subsequent version of Porexpert (as is already the case in Pore-Cor). The simulations have correlation level ranging from 0.15 – 0.30, where 0.0 is a structure in which pores and throats are entirely randomly arranged according to size, and 1.0 is a structure in which sizes are strictly confined to layers grading from one side of the unit cell to the opposite side. To determine the internal structure more reliably, more stochastic realisations of the model must be generated, and the most representative structure must be chosen for which the fitting parameters are closest to the means of all the stochastic generations. (It is invalid to average each fitting parameters separately, because the parameters are coupled by their convergence onto the experimental data.)

Figure 3 shows the void structure of the 15*15*15 ceramic sample 111570127303 which has an experimental porosity of 40.9% and a simulated porosity of 40.8%. The unit cell size has a side length of 2313 µm in the *x*, *y* and *z* directions. The graphics shows voids as solid objects, and the solid

phase as transparent. Much of its detail is invisibly small, although can be seen with Porexpert's virtual reality provision.

The stochastic variations between the simulated structures give rise to different absolute permeabilities. The permeabilities calculated using Porexpert are shown in Table 1 later in the report.

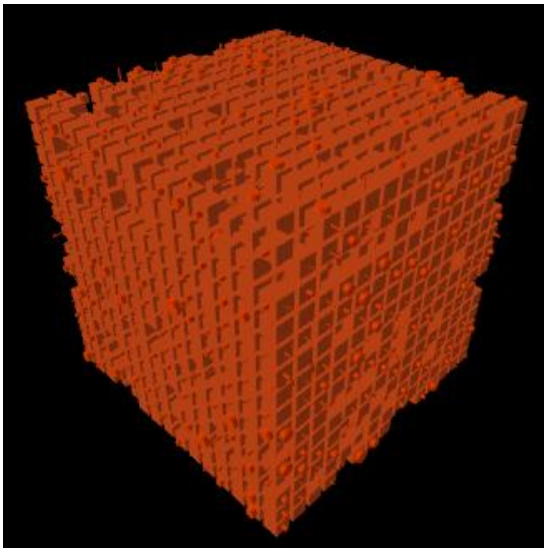

Figure 3. Three dimensional representation of the void structure of ceramic sample 111570127303

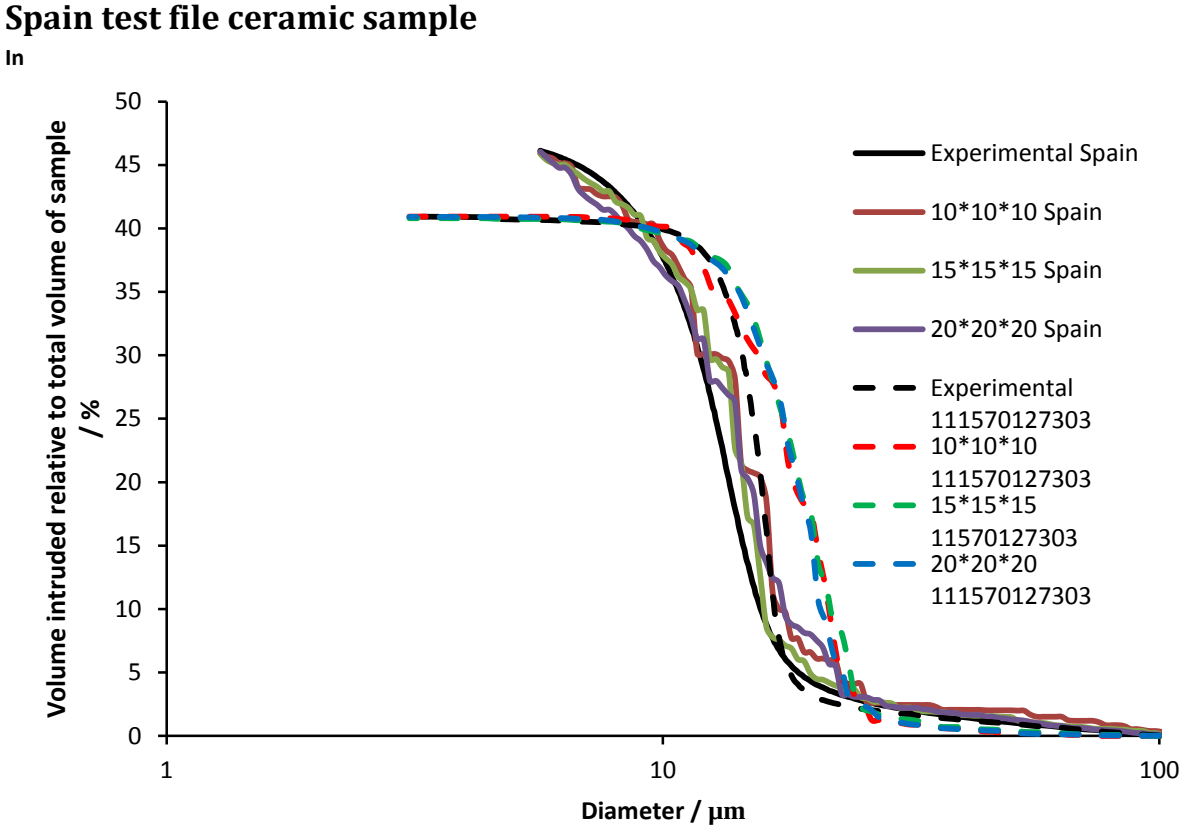

Figure 2 above the simulated fits show good agreement with the experimental data for all unit cell sizes with the vertically banded structure type. In this case, the worst fitting curve had an average distance from the experimental data is 1.67 %. The permeability calculated for the three different unit cells are of a similar magnitude but to obtain a better indication of permeability multiple stochastic realisations are required for each unit cell size to create an indication of permeability range. The calculated permeabilities are detailed in Table 1 for three fluids, a liquid (water), methane and nitrogen.

Figure 4 shows the void structure of the 15*15*15 ceramic sample Spanish test file which has an experimental porosity of 46.1 % and a simulated porosity of 45.9%. The unit cell has a side length of 2151 µm in the *x*, *y* and *z* direction.

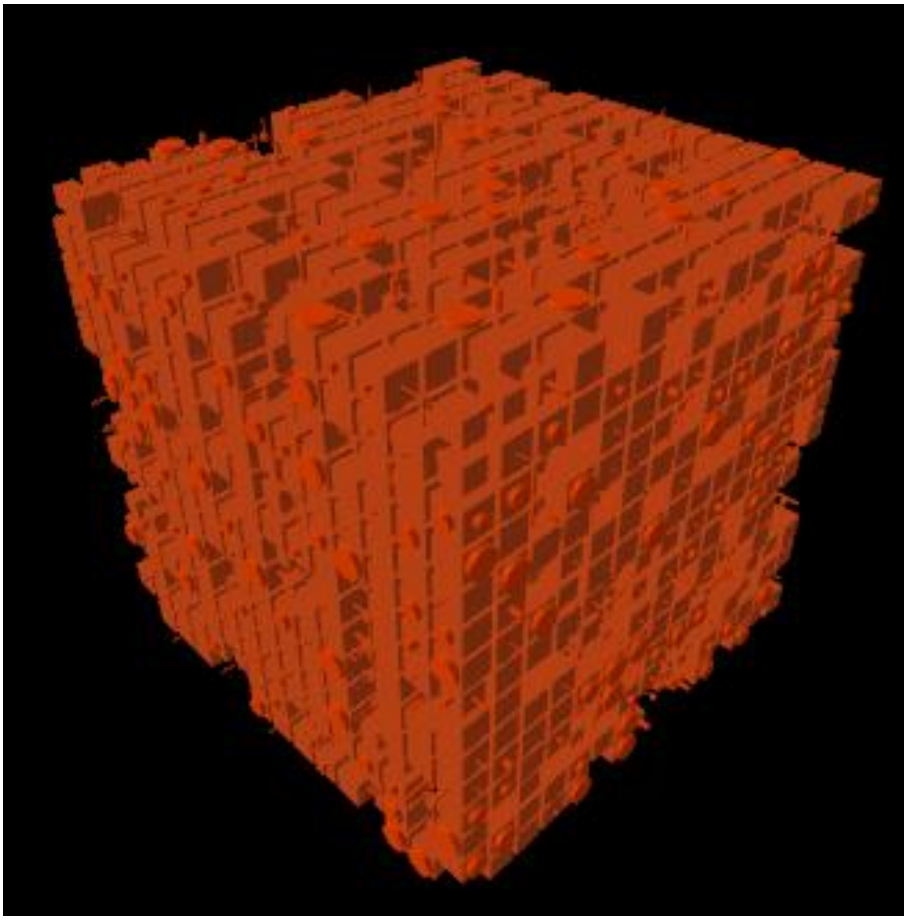

Figure 4. Three dimensional representation of the internal structure of the Spain test file ceramic.

Permeability results

Table 1 Summary of permeability results from the first stochastic generation for three different unit cell sizes for the two ceramic samples. The units of permeability determined by the software have been converted into SI units.

Sample	Unit Cell Size	Fluid	Permeability / m^2
111570127303	10*10*10	Water	1.95E-13
	10*10*10	Methane	2.01E-13
	10*10*10	Nitrogen	2.01E-13
	15*15*15	Water	2.38E-13
	15*15*15	Methane	2.47E-13
	15*15*15	Nitrogen	2.47E-13
	20*20*20	Water	4.88E-13
	20*20*20	Methane	5.08E-13
	20*20*20	Nitrogen	5.08E-13
Spain test file	10*10*10	Water	5.73E-14
	10*10*10	Methane	5.97E-14
	10*10*10	Nitrogen	5.96E-14
	15*15*15	Water	4.45E-14
	15*15*15	Methane	4.71E-14
	15*15*15	Nitrogen	4.70E-14
	20*20*20	Water	8.18E-14
	20*20*20	Methane	8.70E-14
	20*20*20	Nitrogen	8.68E-14

The permeability results shown in Table 1 indicate an order of magnitude difference in the permeability of the samples. The permeability is influenced by the differences in sizes of the voids, which can be visually inferred from the mercury intrusion curves, as well as differences in the fitting parameters such as connectivity and correlation level.

Conclusions

This brief proof-of-concept study summarises some of the capabilities of Porexpert in modelling and comparison of the permeability of ceramic samples. The software predicts permeabilities of similar magnitude to ceramic permeabilities identified in the literature [7], and very much more realistic than permeabilities derived from semi-empirical equations. In this study, the deviations of the simulations of the ceramic sample 111570127303 from the experimental curve are of the same order as the differences between the two experimental curves themselves, so the experimental trend is masked by an inadequately close fit of the simulations. In a full study, a full range of structure types would have to be used over many stochastic generations to improve the fit to the sample 111570127303.

Signed by Technical Director EFMG

Date 21st September 2011

References

1. Gane PAC, Kettle JP, Matthews GP, Ridgway CJ. Void space structure of compressible polymer spheres and consolidated calcium carbonate paper-coating formulations. Ind. Eng. Chem. Res. June 1996;35(5):1753-1764.
2. Gribble CM, Matthews GP, Laudone GM, et al. Porometry, porosimetry, image analysis and void network modelling in the study of the pore-level properties of filters. Chem. Eng. Sci. 2011;66(16):3701-3709.
3. Matthews GP, Laudone GM, Gregory AS, Bird NRA, Matthews AG, Whalley WR. Measurement and simulation of the effect of compaction on the pore structure and saturated hydraulic conductivity of grassland and arable soil. Water Resour. Res. 2010;46(5):W05501.
4. Matthews GP, Moss AK, Spearing MC, Voland F. Network Calculation of Mercury Intrusion and Absolute Permeability in Sandstone and Other Porous Media. Powder Technol. July 1993;76(1):95-107.
5. Bodurtha P, Matthews GP, Kettle JP, Roy IM. Influence of anisotropy on the dynamic wetting and permeation of paper coatings. J. Colloid Interf. Sci. 2005;283:171-189.
6. Ahuja RK, Kodialam M, Mishra AK, Orlin JB. Computational investigations of maximum flow algorithms. European Journal Of Operational Research. 1997;97:509-542.
7. Isobe T, Kameshima Y, Nakajima A, Okada K, Hotta Y. Gas permeability and mechanical properties of porous alumina ceramics with unidirectionally aligned pores. Journal of the European Ceramic Society. 2007;27(1):53-59.

DISCLAIMER

Whilst UoPEL will use all reasonable endeavours to ensure the accuracy of the work performed and any information given, UoPEL makes no warranty, express or implied, as to accuracy and will not be held responsible for any consequence arising out of any inaccuracies or omissions unless such inaccuracies or omissions are the result of negligence on the part of UoPEL or its agents.

The obligations of UoPEL and its agents shall cease upon delivery of the report and no liability whatsoever either direct or indirect shall rest upon them for the effects of any product or process that may be produced or adopted by the client or any other party, notwithstanding that the formulation of such product or process may be based upon the findings of the report.

UoPEL shall not be liable for any death or injury unless it is caused by the negligence of UoPEL or its agents, nor shall it be liable for any loss or damage whatsoever unless it is caused by its wilful default or that of its agents.