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Characterization of synthetic porous media using non–Newtonian fluids: experimental evidence

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Running title: Non–Newtonian fluids for characterizing pore space

Keywords:

Summary: The characterization of pore structures is required for a broad range of applications, from modelling flow dynamics to understanding petroleum reservoir performance. This research was based on a theoretical framework proposed by Abou Najm and Atallah for improved characterization of pore structures using Newtonian and non–Newtonian fluids. Here, we report the first experimental evidence of the ability of non–Newtonian shear thinning fluids to predict the pore structure of three synthetic porous media using only saturated infiltration experiments of water and guar gum solutions at different concentrations. The method predicted multiple distinct representative pore sizes, depending on the number of guar gum solutions used, optimized to mimic the functional behaviour of porous media in terms of flow and porosity. Statistical analysis revealed satisfactory agreement between the predicted and real pore structures in the three synthetic porous media.

30 **Highlights**

- 31 • Experimental evidence of the ability of non–Newtonian fluids to infer the pore structure
32 of porous media
- 33 • Experiments with different guar gum concentrations on three synthetic porous media
34 regenerated known pore structures
- 35 • Experiments enabled extraction of multi–flow regimes mimicking functional flow and
36 porosity behaviour
- 37 • Promising results for an inexpensive and safe new method for pore structure
38 characterization

39

Introduction

Recent advances in imaging techniques have revealed the complexity of the pore microstructure as reflected in its spatiotemporal heterogeneity, scale dependence and tortuous interconnectivity (Bultreys *et al.*, 2016). Modelling flow at the pore scale can be achieved by solving for the governing flow equations (such as Navier–Stokes, lattice Boltzmann, or smoothed particle hydrodynamics) on the scanned complex geometry. However, as sample size increases, technological limitations of imaging and heavy computational costs can deem these methods inefficient. At such meso–scales, modellers can conceptualize complex pore structures into simplified pore network models that maintain similarity in topological features with the modelled porous media (Xiong *et al.*, 2016; Yang *et al.* 2016). Furthermore, as the scale of analysis increases to core, plot, hillslope or beyond, macroscopic models dominate where slow viscous flow is traditionally modelled by Darcy’s law using effective material properties such as porosity and permeability.

To cope with the complexity of the pore structure at the macroscopic scale, different statistical or process–based concepts have developed mostly to account for pore–size distribution (PSD) and connectivity of the pore structure. Those concepts included effective pore radius or bundle of capillary tubes (used for the derivation of equations like the Kozeny–Carman or Hagen–Poiseuille), tortuosity, effective porosity, constriction and dead–end pores (Berg, 2014). Those concepts developed further to account for pore–size variability through fractal models or dual and multiple permeability models. They accounted for connectivity by models including critical path analysis and percolation theory. However, and despite all those attempts, modelling flow and transport processes continues to be a challenge, particularly for complex pore structures or flows associated with non–uniform flow (Sederman *et al.*, 1998; Šimůnek *et al.*, 2003;

Sanders *et al.*, 2012; Stewart *et al.*, 2015).

This means that improving the performance of flow and transport models requires the theoretical and technological development of non-destructive and multiscale methods capable of resolving pore structures. Current characterization methods include stereology, X-ray computer tomography, mercury intrusion porosimetry and low-pressure gas adsorption methods. Each method comes with its own limitations and challenges, leaving much to be desired in the field of pore structure characterization.

Recently, Abou Najm & Atallah (2016) used the properties of non-Newtonian fluids to develop a new theoretical framework for a nondestructive method of functional pore-size characterization of porous media (hereafter referred to as the ANA model). They used the results of N_{fluids} infiltration experiments (with water and $N_{\text{fluids}}-1$ non-Newtonian fluids) to deduce an analogue functional pore structure consisting of N pore-groups of non-interacting representative radii together with their corresponding number and contribution to flow whereby N was set equal to N_{fluids} (note from this point on, N and N_{fluids} are used interchangeably). As long as the complexity of the pore structure can be modelled by the bundle of capillary tubes model, the structure obtained is optimized to mimic the functional behaviour of the real porous medium in terms of flow and porosity. From that point, the PSD could be linked to capillary pressure and hydraulic conductivity.

A similar study was done by Rodriguez de Castro *et al.* (2014, 2016) whereby the bundle of straight parallel capillaries was also adopted to represent porous media. In their research, they formulated a set of inequalities from which they were able to attain pore sizes and their corresponding numbers. Their general methodology relied on applying increasing pressure

gradient increments of a Herschel–Bulkley fluid and noting that for such fluids, flow does not occur below a certain critical radius.

In comparison, the ANA model constructed weights and radii of the derived pore structure so as to satisfy the water (Newtonian) flow equation while being constrained by the effect of porosity and the $(N-1)$ non-Newtonian flow equations. The ANA model then relied on the intrinsic nonlinearity in non-Newtonian fluids to attain those weights and radii and therefore a PSD. The ANA model applies to a wide range of viscosity models to allow for a wide range of non-Newtonian fluid combinations. These non-Newtonian fluids need not be different all the time because testing with the same fluids at different pressure heads or concentrations (except for power-law fluids) generates new unique signatures for every new fluid–pressure gradient and/or fluid–concentration combination.

Both methods adopted a simple pore structure model (bundle-of-tubes) for pore structure characterization. We realize that there has been considerable criticism to the representation of pore structure of complex porous media with the bundle-of-tubes concept (Balhoff & Thompson, 2006; Sheffield & Metzner, 1976; Duda *et al.*, 1983). More complex models including network models have been used to model shear-thinning flow in porous media (Lopez *et al.*, 2003; Balhoff & Thompson, 2004, 2006). Such models can provide improved representation of complex pore structures, but require more inputs and their formulation remains an open theoretical and experimental challenge.

In this paper, we present the first experimental evidence that validates the ability of a non-Newtonian fluid at different concentrations to infer the pore structure of simple and synthetic porous media using the ANA model. We apply infiltration tests using water and different guar gum solutions on three synthetic porous media (Figure 1) made with different

108 sizes, numbers and combinations of capillary tubes. Using the outputs of these infiltration tests
109 (saturated flows, Q), we aim to answer the following questions: (i) can the results of N
110 experiments using water and $(N-1)$ Newtonian fluids be used to compute N different
111 representative pore sizes and their corresponding contribution to flow for these particular
112 synthetic porous media? and (ii) can the results of N experiments using water and $(N-1)$ non-
113 Newtonian fluids be used to compute N different representative pore sizes and their
114 corresponding contribution to flow for these synthetic porous media? We demonstrate
115 experimentally that the answer to the first question is no, whereas the answer to the second
116 question is yes.

Materials and methods

The constant viscosity (η) in Newtonian fluids makes flow (Q) proportional to the fourth power of the tube radius (r^4) and hydraulic gradient (dP/dz) (the Hagen–Poiseuille law). Therefore, testing with different Newtonian fluids on the same pore structure generates flows proportional to the inverse of their corresponding viscosities (given same pressure gradient), rendering no additional information regarding the pore structure. However, testing with non–Newtonian fluids that have non–constant viscosity terms (function of the strain rate) leads to flows (Q) that are no longer proportional to a constant power of pore size and hydraulic gradient. The ANA model demonstrated theoretically that testing with different non–Newtonian fluids (or the same fluid at different pressure gradients or concentrations) on the same pore structure will generate new unique signatures for every new fluid–pressure gradient and/or fluid–concentration combination (except for the power law viscosity models), thus allowing us to infer additional information about the pore structure. Here, we present the methodology of the first experimental validation.

Experimental set–up

Three different combinations of numbers and pore radii of capillary tubes were selected (Table 1) to formulate three synthetic pore models (SPMs). For each SPM, two 64–mm diameter acrylic discs were perforated and assembled with a threaded metal rod to form the upper and lower bounds of the SPM (Figure 1a). Capillary tubes were 100–mm long, and were carefully placed into the disc perforations to create the pore structure of the three SPMs (Figure 1b). A combination of four, three and two radii (Table 1) were adopted to create SPM–1, SPM–2 and SPM–3, respectively. This was followed by injection of liquid silicon around the insertion points

of the tubes to hold them in place (Figure 1c). Once the liquid silicon had dried, Teflon was wrapped around the outer perimeter of the discs to restrict fluid flow in the space between the permeameter and disc during the infiltration experiments.

Each SPM was placed in the permeameter chamber and saturated with the fluid (water and the non-Newtonian guar gum concentrations). The fluid was then allowed to flow into a flask placed on a balance. For each test (using water and $N-1$ different guar gum concentrations, j), the rate of mass flow and head (accounting for gravity) were recorded once a constant pressure head was achieved. The rate of volumetric flow (Q_j) for each fluid j was calculated as $(\Delta m / \rho_j) / \Delta t$ where: Δt is the change in time in s, Δm_j is the change in mass in kg of fluid S_j over a time interval Δt , ρ_j is the density in kg m^{-3} of fluid j and Q_j is the rate of flow in $\text{m}^3 \text{s}^{-1}$ of fluid S_j .

Liquid solutions

Deionized water and guar gum solutions at different concentrations were chosen as the N fluids to test the theory on the SPM. Here, water is the Newtonian fluid with density and dynamic viscosity of 997 kg m^{-3} and $9 \times 10^{-4} \text{ Pa s}$ respectively at 25°C , maintained throughout the experimental process.

Different concentrations of guar gum solutions represent the non-Newtonian shear-thinning fluids in our experiment. These solutions were prepared by adding dry guar gum powder to containers of deionized and degasified water and allowing the contents to mix overnight at 230 revolutions per minute (rpm) using a shaker and then stored at 4°C for 12 hours. The 2.75, 4.6 and 7.2 kg m^{-3} solutions were prepared by diluting a 10 kg m^{-3} solution. Densities of the guar gum and parameters of the Cross (1965) viscosity model (Equation (1)) were calculated by linear interpolation from the values recommended by Chenlo *et al.* (2010) (Table 2).

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + k \left(\frac{dv_z}{dr} \right)^{1-n}}, \quad 0 < r < R \quad (1)$$

where $\frac{dv_z}{dr}$ is the shear rate in m s^{-1} , r is a variable in m varying between 0 and R (radius of the capillary tube), η_0 and η_{∞} are the zero and the infinite shear rate viscosities in Pa s , respectively, k is the time constant (s^{1-n}) and n is the dimensionless exponent.

Theory and numerical modelling

The governing differential equation for modelling flow in round capillary tubes (neglecting tortuosity) is:

$$\frac{1}{r} \frac{d}{dr} \left(r \eta \frac{dv_z}{dr} \right) = \rho g \left(\frac{dh}{dz} - 1 \right) = H, \quad (2)$$

where g the gravitational acceleration in m s^{-2} , $\frac{dh}{dz}$ is the pressure head gradient and H is equal to $\rho g \left(\frac{dh}{dz} - 1 \right)$ in $\text{kg m}^{-2} \text{s}^{-2}$. For horizontal flow, the governing differential equation is the same as Equation (2) but with the right-hand side (H) equal to $\rho g \frac{dh}{dz}$.

Abou Najm & Atallah (2016) used Equation (2) to obtain the velocities of different fluids (S_j) in porous media consisting of vertical circular tubes of various sizes and numbers, then used Equation (3) for flow calculation:

$$Q_j = \sum_{i=1}^N X_i \left[2\pi \int_0^{R_i} r v^{S_j} dr \right], \quad j = 1, 2, \dots, N_{\text{fluids}} \quad (3)$$

where X_i is the number of pores of radius R_i , v^{S_j} is the velocity for fluid S_j and Q_j is the total flow in the porous medium from fluid S_j , representing the output from infiltration experiments.

We note that it is sufficient for some liquid solutions to be tested at different concentrations and/or pressures to qualify as different fluids and be part of the N_{fluids} considered in the ANA model. In fact, we used different concentrations of guar gum solutions as our different $N-1$ non-Newtonian fluids. Furthermore, changing the pressure head, but using the same guar gum concentration can be enough to provide the additional signatures used by the proposed theory. Abou Najm & Atallah (2016) coupled the equation of structure (Equation (4)) and N flow equations (Equation (3), recall $N_{\text{fluids}} = N$) to form a system of $N \times N$ equations (Equation (6)). They used Equation (3) for all fluids and Equation (5) for water flow after setting flow from water as fluid 1 (Q_1).

$$\phi A_T = \sum_{i=1}^N X_i \pi R_i^2, \quad (4)$$

$$w_i Q_1 = X_i C_1 R_i^4, \quad (5)$$

where A_T is the total cross-sectional area of the porous medium sample, w_i is the fraction of water flow contributed by each pore radius R_i (such that $\sum_{i=1}^N w_i = 1$ and $w_i > 0$), $C_1 = \frac{\pi}{4} \left(-\frac{H_1}{2\mu} \right)$, μ is the constant viscosity of water and H_1 is the head term for the water experiment.

$$\underbrace{\begin{bmatrix} \frac{2\pi \int_0^{R_1} r v^{S_2} dr}{R_1^4} & \frac{2\pi \int_0^{R_2} r v^{S_2} dr}{R_2^4} & \frac{2\pi \int_0^{R_3} r v^{S_2} dr}{R_3^4} & \dots & \frac{2\pi \int_0^{R_N} r v^{S_2} dr}{R_N^4} \\ \frac{2\pi \int_0^{R_1} r v^{S_3} dr}{R_1^4} & \frac{2\pi \int_0^{R_2} r v^{S_3} dr}{R_2^4} & \frac{2\pi \int_0^{R_3} r v^{S_3} dr}{R_3^4} & \dots & \frac{2\pi \int_0^{R_N} r v^{S_3} dr}{R_N^4} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{2\pi \int_0^{R_1} r v^{S_N} dr}{R_1^4} & \frac{2\pi \int_0^{R_2} r v^{S_N} dr}{R_2^4} & \frac{2\pi \int_0^{R_3} r v^{S_N} dr}{R_3^4} & \dots & \frac{2\pi \int_0^{R_N} r v^{S_N} dr}{R_N^4} \\ \frac{2\pi \int_0^{R_1} r dr}{R_1^4} & \frac{2\pi \int_0^{R_2} r dr}{R_2^4} & \frac{2\pi \int_0^{R_3} r dr}{R_3^4} & \dots & \frac{2\pi \int_0^{R_N} r dr}{R_N^4} \end{bmatrix}}_A \underbrace{\begin{bmatrix} w_1 \\ w_2 \\ w_3 \\ \vdots \\ w_N \end{bmatrix}}_w = \underbrace{\begin{bmatrix} \frac{Q_2 C_1}{Q_1} \\ \frac{Q_3 C_1}{Q_1} \\ \vdots \\ \frac{Q_N C_1}{Q_1} \\ \frac{\phi A_T C_1}{Q_1} \end{bmatrix}}_b \quad (6)$$

Note that this form of Equation (6) neglects tortuosity because all capillary tubes were straight with no curves (the more general form was derived and presented in Abou Najm & Atallah, 2016). Equation (6) was then solved simultaneously and numerically to provide answers to the following three problems—types given the total saturated rates of flow (Q_j) from the constant head infiltration experiments:

1. *Problem–Type 1:* Given the predefined structure represented in N different pore radii, (R_i), what are the corresponding weights (contributing to flow) of each radius (w_i)? Here, information is available for matrix **A** in Equation (6) and we solve for vector **w** given vector **b** (which contains experimental results of N flow experiments).
2. *Problem–Type 2:* Given pre-defined flow weights ($w_1, w_2, \dots, w_N$ of total flow Q), what are the pore radii (R_i) corresponding to each flow regime ($w_i Q$)? Here, information is available for vector **w** in Equation (6) and we solve for the radii in matrix **A** given vector **b**.
3. *Problem–Type 3:* More generally, how can flow be attributed to N representative pore radii (R_i) together with their corresponding contributions to flow (w_i). Here, we solve for the radii in matrix **A** and weights in vector **w** given vector **b**.

This is similar in concept to the average pore size (Sheffield & Metzner, 1976; Duda *et al.*, 1983, Koponen *et al.*, 1997; Auriault *et al.*, 2002) which is currently the basis of many hydrologic and flow models (but here with N average pore sizes). The average pore size came as a result of experimentally using only water ($N=1$), and therefore could only obtain one averaged pore size. The proposed generalized model can provide N representative and physically based pore sizes from N different fluids.

Preliminary Test

Before proceeding with validation of the ANA model, the overall performance of the infiltration experiments was assessed by comparing the theoretical and experimental total flows for the three SPMs. This was necessary to ensure that the results of the constant head experiments are in close accord with the expected theoretical flows for water and the $N-1$ guar gum solutions (Table 3). Theoretical flows were obtained through numerical integration of Equations (1–3) using the number of tubes and dimensions in Table 1 and the fluid characteristics in Table 2. Experimental flows were calculated from the N infiltration experiments for each SPM. Equation (7) was used to calculate the relative error between the theoretical and experimental flows:

$$\%Error = \frac{Q_{Experimental} - Q_{Theoretical}}{Q_{Experimental}} \times 100, \quad (7)$$

In general, the experimental and theoretical flows were in agreement as shown in Table 3 with errors ranging between 2.17 and 2.44% for water and between 3.86 and 6.01% for the guar gum concentrations. While the errors in flow for both water and guar gum concentrations are less than 6%, it is worth mentioning that those errors are consistently higher in guar gum concentrations than water for all SPMs. Potential sources for these minor errors in the guar gum concentrations could be the adoption of parameters from Chenlo *et al.* (2010), which might not have been completely representative of the guar gum used in this experiment (being a natural product, with characteristics subject to the quality of the used and methods of commercial preparation). More accurate results could possibly be achieved by characterizing the different concentrations of guar gum with a rheometer.

239 *The ANA model experimental validation*

240 For each SPM, we used the results of the infiltration experiments (Q_j) to solve Equation (6)
241 numerically and determine the representative radii and their corresponding weights. Equation (6)
242 was solved three times for each SPM to evaluate its performance in solving for the three
243 problem-types.

244 To test the performance of the proposed model, we compared the functional performance of the
245 estimated pore structure to the real one using two criteria: one for saturated flow behaviour and
246 the other for unsaturated characteristics. For saturated flow behaviour, we plotted the infiltration
247 depths of water (at a given time) given the real radii of the three SPMs and compared them with
248 those predicted from the ANA model (using different guar gum solutions). For the unsaturated
249 characteristics, we derived the water release curves for the three SPMs (using the Young–
250 Laplace Equation) and compared it to the ones predicted from the ANA model (using different
251 guar gum solutions).

252 To quantify the performance of the predicted pores, various standard statistical tests were
253 adopted to compare the model's ability to mimic the functional behaviour of the SPMs tested.
254 Three standard statistical tests were used, namely: the absolute percent relative error (APRE), the
255 Nash–Sutcliffe efficiency coefficient (NSE) and the percent bias (PBIAS).

256 The APRE measures the total relative error between the simulated ($N=1$ and proposed model)
257 and the real pores. The closer the APRE is to zero, the better the performance of the model. This
258 was calculated according to Equation (8):

259
$$APRE = 100 \times \frac{\sum_{k=1}^K |X_{sk} - X_{rk}|}{\sum_{k=1}^K X_{rk}}, \quad (8)$$

260 where K is the total number of subintervals over the entire domain, X_{rk} is the real quantity over
261 interval k , X_{sk} is the simulated quantity over interval k .

262 The Nash–Sutcliffe efficiency coefficient (NSE) is a standard statistic that assesses the model's
263 goodness-of-fit relative to the observed data by calculating the relative magnitude of the
264 residual variance (noise) compared to the observed data variance as expressed in Equation (9)
265 (Nash & Sutcliffe, 1970):

$$266 \quad NSE = 1 - \frac{\sum_{k=1}^K (X_{sk} - X_{rk})^2}{\sum_{k=1}^K (X_{rk} - \bar{X}_r)^2}, \quad (9)$$

267 where $\bar{X}_r$ is the mean of the observed quantity. The NSE values range from $-\infty$ to 1; values
268 closer to 1 indicate better model simulation of the observed data.

269 The PBIAS is a measure of the tendency of the model to under- or over-predict the observed
270 data and is expressed as a percentage in Equation (10)

$$271 \quad PBIAS = 100 \times \frac{\sum_{k=1}^K (X_{sk} - X_{rk})}{\sum_{k=1}^K X_{rk}}. \quad (10)$$

272 A positive PBIAS indicates a tendency for the model to overestimate the data whereas a negative
273 PBIAS is the exact opposite.

274 **Results and discussion**

275 The SPMs made with different sizes and numbers of capillary tubes were used to demonstrate
276 the ability of non-Newtonian fluids to characterize porous media. This is the first experimental
277 validation, which is necessary before extending the concept to more complex porous media such
278 as real soil or fractured rocks in order to make sure that the variation within common and
279 practical concentrations of non-Newtonian fluids can provide enough distinct and unique

signatures to distinguish between practical ranges of pore sizes. Once validated, the ANA model can be tested with real porous media and extended to different applications using any of the three problem-types.

How effective are non-Newtonian fluids are?

The results showed that non-Newtonian fluids are indeed effective. Experimental flows for water and guar gum ($N-1$ different concentrations) were used to calculate the corresponding contribution to flow from fixing the radii R_i to the actual ones (in Problem-Type 1), or to calculate the radii while fixing the weights w_i to the actual ones (in Problem-Type 2) for the three SPMs. Table 4 shows the results of the weights obtained (in Problem-Type 1) and radii obtained (in Problem-Type 2), in addition to their respective actual values. This provides a proper assessment of the ability of non-Newtonian fluids to reproduce the functional flow behavior of the porous media.

For Problem-Type 1, the use of $N-1$ guar gum concentrations as non-Newtonian fluids allowed us to determine that SPM-1 is governed by only two radii, namely the 0.4- and 1-mm. The 1-mm radius has a predicted weight contribution of 60.3%, approximately equal to the actual one of 62.5%. The model also identified the total contribution of the 0.4- and 0.5-mm radii, by predicting that they hold the remaining 40%. However, it over-predicted the contribution of the 0.4-mm and under-predicted that of the 0.5-mm radii. Here, the small difference between the 0.4- and 0.5-mm radii could potentially be the reason for this error, in addition to the slight differences between the experimental and theoretical flows (Table 3). The latter could be a byproduct of a discrepancy between the modelled and actual viscosity model for the guar gum concentrations. Furthermore, the large molecular weight of guar gum (in the range of 10^6 g mol^{-1}) can be another possible reason for explaining the error in differentiating between two pores

with a difference of 0.1-mm spacing. A similar reasoning can be attributed to SPM–2, whereby merging the weight contributions of the 0.4- and 0.5-mm radii resulted in a total flow contribution of 0.45 which was close to the actual weight contribution of 0.52 (Table 4).

The same conclusion can be inferred from Problem–Type 2, whereby the weights were fixed to the actual ones and then the radii were calculated. For example, the radii in SPM–1 (the 0.4- and 0.5-mm radii) were merged into 0.4-mm rendering it and the 1-mm radii as the only two major contributing sources of flow (these results were relatively similar to those obtained for Problem–Type 1). On the other hand, the 0.4- and 0.5-mm actual radii for SPM–2 were merged into an optimized 0.45-mm radius after the simulations had been done. As for SPM–3, there was close agreement between the actual (0.5- and 1.0-mm) and predicted (0.55- and 0.81-mm).

Needless to say, any combination of only Newtonian fluids cannot predict the pore structure of these SPM irrespective of the number of Newtonian fluids used. The reason is that the columns of matrix **A** of Equation (6) become linearly dependent because flow in Newtonian fluids is a function of the fourth power of pore size irrespective of fluid viscosity (the Hagen–Poiseuille law).

Assessment of infiltration depth

The previous section validated the weights given the actual radii (Problem–Type 1) and radii given the actual weights (Problem–Type 2) for all SPM. However, the ANA model does not assume prior knowledge of the actual radii or their weights. So to demonstrate the capability of the model, we redid all the simulations assuming different radii and weights as inputs for Problem–Types 1 and 2, respectively. As for Problem–Type 3, it solves for radii and weights simultaneously without the need for inputs from the user other than a starting point for the radii (further discussions on Problem–Type 3 are included below).

We also changed the number of guar gum solutions from N to $N-1$ and $N-2$ (when applicable), therefore, we also estimated the dominant radii for $N-1$ and $N-2$ (Problem-Type 1), the weights (Problem-Type 2) or both (Problem-Type 3) for all three SPMs. The results of all the simulations for the three problem-types, three SPMs and with N , $N-1$, $N-2$ guar gum solutions (when applicable) are presented in Table S1 (Supporting Information).

The results in Table S1 were used to calculate the average velocities of the representative pores (generated from the three problem-types) so that we can compare them with that of the real pores (Figure 2). The average velocity is given by Equation (11) and the cumulative pore area was calculated by summing the cross-sectional area from the smallest radius to the largest.

$$q_k = \frac{Q_{1k}}{A_k} = \frac{X_k C_1 R_k^4}{X_k \pi R_k^2} = \frac{C_1 R_k^2}{\pi}. \quad (11)$$

For comparison, average velocities calculated using a single representative pore radius ($N = 1$ estimated from the Hagen-Poiseuille law using total flow) were also added to the plots in Figure 2. For each of the plots in Figure 2, the APRE, NSE and PBIAS statistics were calculated relative to the pore volume (which is the variable of interest) and summarized in Table 5. A similar exercise was done by plotting the average velocity against cumulative percent flow (Figure S1) and whose APRE, NSE and PBIAS statistics are summarized Table S2.

The results from Table 5 and Figure 2 showed the ability of the proposed model to predict flow, in particular when compared with results of the baseline of $N = 1$. For example, the APREs of the $N = 1$ scenario corresponding to the three SPMs were 85.61, 60.73 and 62.56%, respectively, whereas the APREs ranged between 24.46 and 60.00% for all problem-types, number of guar gum solutions and SPMs. The worst performance with the new method was for SPM-2 with Problem-Type 1 ($N=2$ and $N=3$) with APREs of 51.28% ($N=3$) and 60% ($N=2$). Note that these

two errors can be attributed to the choice of radii because errors can be reduced further by performing additional simulations with different radii. The proof of the prior statement is evident when examining the APRE values for Problem–Types 2 and 3, whereby the errors decreased to 35.87 and 39.76% ($N=3$), respectively, and to 25.64 and 30.20%, respectively ($N=2$).

The Nash–Sutcliffe efficiency coefficient (NSE) of the three problem–types ranged between 0.17 and 0.86, which substantially outperformed the $N = 1$ scenario with NSEs ranging between -0.000035 and -0.0011 . The NSE improved in most of the cases and problem–types as N increased, which was expected because increasing N improves ability to resolve more detail in the pore structure, thus the functional behavior of the flow.

In terms of PBIAS, its value for both the $N = 1$ scenario and proposed models should be zero because the weights represent the proportion of water flow controlled by their respective radii, and their sum was constrained to one (Abou Najm & Atallah, 2016). However, because of the minor differences between theoretical and experimental flows (Table 3), there were some minor deviations of up to 2.71%. Regardless, it can be inferred that the ANA model does not improve estimates of flow and pore structure at the expense of increasing the bias.

Assessment of porous medium water release curve

All experiments were done under saturated conditions, but the additional unique signatures obtained from experiments with $N-1$ guar gum concentrations enabled us to estimate the water release curves and predict the unsaturated behaviour of those SPMs. Figure 3 shows the water release curves of the three SPMs as well as those obtained for $N=M$, $N=M-1$, $N=M-2$ and $N=1$ radii using the Young–Laplace equation (Equation (12)) where M is the number of actual pore sizes for each SPM, and was 4, 3 and 2 for SPM–1, SPM–2, and SPM–3, respectively.

$$|\psi_i| = \frac{2\sigma \cos \theta}{\rho g R_i}, \quad (12)$$

where ψ_i is the suction head for pore radius R_i , σ is the surface tension of water and θ is the water–air contact angle. In what follows, we assumed a surface tension $\sigma = 0.07191 \text{ J m}^{-2}$, a water density $\rho = 997 \text{ kg m}^{-3}$ and a contact angle $\theta = 0^\circ$.

The closer agreement between real (Table 1) and estimated porous medium water release curves (Figure 3) using the ANA model (the red lines in Figure 3) as compared to the curve based only on the average pore radius (the blue line in Figure 3) shows the effectiveness of the proposed model in predicting unsaturated behaviour from experiments under saturated conditions.

Problem–Type 3: Uniqueness of solution

Although the solutions generated from Problem–Types 1 and 2 are unique, the same cannot be said for Problem–Type 3 because we have N equations with $2N$ unknowns (radii and their corresponding weights). Thus, to validate the approach, we generated 25 different PSD for each of SPM–1 and SPM–2 from 25 different starting radii R_i^0 . Figure 4 displays the results of the actual pores of SPM–1 and SPM–2 by the red crosses (calculated from Table 1) and the 25 PSDs generated from Problem–Type 3 by the wide array of markers.

The four and three representative radii calculated from solving Problem–Type 3 for SPM–1 and SPM–2, respectively were clustered around the radii of the actual pores. This provides strong validation for the model and shows that while theoretically we have an infinite number of possible solutions, they all cluster around the actual values and provide a functional characterization of the pore structure as optimized for flow and porosity.

392

393 **Conclusion**

394 We presented the first experimental evidence that demonstrated the ANA model's
395 effectiveness in predicting the pore structure of three SPMs created from different combinations
396 of capillary tube sizes. We demonstrated experimentally the ability of water and $N-1$ shear
397 thinning non-Newtonian fluids to provide N representative pore radii and their contributions to
398 flow. This unique and distinct signature (N representative pore radii) was obtained from every
399 addition of a guar gum concentration. Summing up those signatures enabled the prediction of
400 additional information about the pore structure within the practical range of variation in
401 properties of different guar gum concentrations. As such, the practicality of the proposed
402 method, as revealed experimentally on simple SPMs, opens the door for testing on real complex
403 soils or fractured rocks. It is now possible to extend the development of the theoretical model to
404 incorporate more advanced pore structure models including fractals, percolation theory, or 2-D
405 and 3-D flows using a network representation of the porous medium. We hope that this work has
406 demonstrated the potential of using non-Newtonian fluids as a means to characterize simple
407 porous media. Future attempts should target to extend the use of the ANA model into real porous
408 media applications. As such, porous media characterization can be added to the wide range of
409 potential applications of non-Newtonian fluids in natural soils such as for soil remediation all the
410 way to enhanced oil recovery from underground reservoirs.

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Tables

Table 1 Synthetic soil characteristics (tube length=100 mm, total volume=32 1700 mm³)^a.

SPM	Radii /mm	Number	Porosity	% of total porosity
1	0.25	45	0.0095	28.96
	0.40	15		24.71
	0.50	10		25.74
	1.00	2		20.59
2	0.40	25	0.0120	32.65
	0.5	25		51.00
	1.00	2		16.35
3	0.50	30	0.0092	78.95
	1.00	2		21.05

^aPore radii were selected based on availability and suitability to the experiment. Micropores were avoided to eliminate risk of filtration of guar gum.

SPM, synthetic pore model.

481 **Table 2** Densities and Cross (1965) parameters of the three guar gum concentrations, with Cross
482 model parameters obtained from Chenlo *et al.* (2010)

Concentration	Density	η_0	η_∞	K	N
/kg m ⁻³	/kg m ⁻³	/Pa s	/Pa sE-09	/s ¹⁻ⁿ	
2.75	997	0.088	1.65	0.0410	0.280
4.60	1000	0.580	4.00	0.1300	0.310
7.20	1002	2.753	8.21	0.2591	0.266

483 η_0 , zero shear rate viscosity; η_∞ , infinite shear rate viscosity; k , time constant; n , dimensionless
484 exponent.

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486 **Table 3** Summary of theoretical and experimental flows. Theoretical flows were numerically
487 integrated (Equations (1–3)) using tube characteristics of the three SPMs (Table 1).

SPM	Pore classes	Guar gum concentration	Head	Theoretical flow	Experimental flow	Relative error
		/kg m ⁻³	/mm	/m ³ s ⁻¹ E-03	/m ³ s ⁻¹ E-03	/ %
1	4	0.00 (deionized water)	43	0.01940000	0.0198300	2.17
		2.75	130	0.00112300	0.0010790	-4.08
		4.60	430	0.00060200	0.0006277	4.09
		7.20	350	0.00006055	0.0000583	-3.86
2	3	0.00 (deionized water)	37	0.02457000	0.0239100	-2.76
		4.60	250	0.00030000	0.0003153	4.85
		7.20	250	0.00004660	0.0000444	-4.95
3	2	0.00 (deionized water)	45	0.02398000	0.0245800	2.44
		2.75	50	0.00058200	0.0005490	-6.01

488 SPM, synthetic pore model.

Table 4 Summary results of the three problem–types with same radii and weights as in the experimental setup^a

Problem–type	SPM	Radii /mm	Weights	Number of pores	Actual weights	Difference /%
1	1	<u>0.25</u>	0.000	0.00	<u>0.055</u>	–0.055 (–100.0)
		<u>0.40</u>	0.362	45.72	<u>0.120</u>	0.242 (201.0)
		<u>0.50</u>	0.035	1.80	<u>0.200</u>	–0.165 (–83.0)
		<u>1.00</u>	0.603	1.95	<u>0.625</u>	–0.022 (–3.5)
	2	<u>0.40</u>	0.286	45.70	<u>0.150</u>	0.136 (91.0)
		<u>0.50</u>	0.165	10.80	<u>0.370</u>	–0.205 (–55.0)
		<u>1.00</u>	0.549	2.25	<u>0.480</u>	0.069 (14.0)
	3	<u>0.50</u>	0.489	31.07	<u>0.484</u>	0.005 (1.0)
		<u>1.00</u>	0.511	2.03	<u>0.516</u>	–0.005 (–1.0)
					Actual Radii /mm	Difference /mm (%)
2	1	0.40	<u>0.055</u>	7.10	<u>0.250</u>	0.150 (60.0)
		0.40	<u>0.120</u>	15.50	<u>0.400</u>	0.000 (0.0)
		0.40	<u>0.200</u>	25.10	<u>0.500</u>	–0.100 (–20.0)
		0.98	<u>0.625</u>	2.20	<u>1.000</u>	–0.020 (–2.0)
	2	0.45	<u>0.150</u>	15.00	<u>0.400</u>	0.050 (12.5)
		0.45	<u>0.370</u>	36.50	<u>0.500</u>	–0.050 (–10.0)
		1.05	<u>0.480</u>	1.60	<u>1.000</u>	0.050 (5.0)
	3	0.55	<u>0.484</u>	21.20	<u>0.500</u>	0.050 (10.0)
		0.81	<u>0.516</u>	4.76	<u>1.000</u>	–0.190 (–19.0)

^a(underlined and regular numbers represent what is given and what is solved for, respectively)

SPM, synthetic pore model.

Table 5 Pore volume error summary of the three problem-types relative to cumulative pore volume

Problem-type	Statistical measures	SPM-1			SPM-2		SPM-3
		4 Radii	3 Radii	2 Radii	3 Radii	2 Radii	2 Radii
1	APRE/%	44.05	47.27	47.28	51.28	60.00	39.53
	NSE	0.61	0.58	0.58	0.38	0.17	0.51
	PBIAS /%	1.96	2.00	−0.18	−2.71	−2.68	2.48
2	APRE /%	41.00	25.37	32.93	35.87	25.64	37.12
	NSE	0.66	0.84	0.70	0.50	0.72	0.53
	PBIAS /%	1.98	2.00	2.04	−2.70	−2.69	2.48
3	APRE /%	24.46	36.33	34.20	39.76	30.20	42.10
	NSE	0.86	0.72	0.68	0.46	0.57	0.37
	PBIAS /%	1.95	2.00	2.05	−2.69	−2.69	2.48
N = 1	APRE /%	85.61000			60.730		62.5600
	NSE	−0.00035			−0.001		−0.0011
	PBIAS /%	2.040000			−2.690		2.48000

SPM, synthetic pore model; APRE, absolute percent relative error; NSE, nash–sutcliffe efficiency

coefficient; PBIAS, percent bias.

Figures

Figure 1: Schematic diagram of experimental setup

Figure 2: Average velocity plotted against cumulative pore area from applying (a) problem-type 1 (column 1), (b) problem-type 2 (column 2) and (c) problem-type 3 (column 3) on SPM-1 (row 1), SPM-2 (row 2) and SPM-3 (row 3). In problem-type 1, equation (3) was solved for the weight vector w_i given the radii under a minimum weight constraint of 2.5% ($w_{\min}$). In problem-type 2, given the weights w_i , the radii R_i were calculated for each SPM. Finally, in problem-type 3, both the radii R_i and the weights w_i were calculated under a $w_{\min}$ of 2.5%, minimum inter-radial spacing (d_{adj}) of 1.2 and maximum ratio between the largest and smallest radius of 10 (d_{range}).

Figure 3: The porous medium water release curves of the three synthetic soils and those obtained for $N=M$, $N=M-1$, $N=M-2$ and $N=1$ radii with the three problem-types.

Figure 4: Cumulative water flow by weight for: (a) SPM-1 and (c) SPM-2. Cumulative pore-size distribution for: (b) SPM-1 and (d) SPM-2. Each similar symbol signifies a single scenario out of the 25 different starting points.

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