Simulation of the Intrusion Process and Extrusion of Non-Wetting Liquid From Porous Media in Quasi-Static Mode

V A Byrkin\textsuperscript{1,2} and A V Geraseva\textsuperscript{1}

\textsuperscript{1}National Research Nuclear University MEPhI, Kashirskoe sh. 31, Moscow, 115409 Russia
\textsuperscript{2}Polymeric Membranes Laboratory, A.V. Topchiev Institute of Petrochemical Synthesis, RAS, Leninsky prospekt 29, Moscow, 119991, Russia

E-mail: vabyrkin@mephi.ru

Abstract. To understand the thermodynamics, transport and physical phenomena in porous media today, the most effective way is to use various models of porous media and conduct numerical experiments on their basis. It has been shown that such models are an effective tool for research of transport processes from the local scale at the level of individual pores to the level of individual granules. The approach proposed in this paper is based on numerical calculations based on known theoretical approaches. The principal difference from the previously used approaches and novelty lies in the absence of simplifications associated with the narrowing of the distribution of pores in size and the number of nearest neighbors, which allows us to take into account in detail the possible geometric configurations, when the pore of the same radius can be surrounded by a different number of neighboring pores. In addition, the use of numerical modelling allows us to obtain a large number of different parameters, ranging from structural characteristics (the number of nearest neighbors, connectivity, etc.), cluster (percolation thresholds) and ending with volume dependencies on pressure and time and the visualization of filling processes.

1. Introduction
Over the past decades, due to the complexity of the real pore structure, many experimental, theoretical and numerical approaches have been proposed and developed to study transport processes through porous media [1-11]. Field experiments, as well as studies using X-rays, PEM, SEM, etc., are usually expensive and time-consuming. Such measurements are sensitive to material composition, sample preparation and methodology. Analytical solutions are usually limited to problems with perceived homogeneous properties and specific boundary conditions, some of which are of limited practical significance or difficult to assess.

Modelling a porous environment, or a numerical approach, can significantly improve the understanding of large-scale processes and determine the physical nature of phenomena. Their importance is related to the fact that they can provide rather economical and accurate forecasts for local transport (diffusion/permeability) and at the same time allow systematic changes in system parameters (pore geometry, fluid properties and boundary conditions), which is much more difficult to achieve through experiments [12].

To build a model of a porous medium it is necessary to know the geometry and topology of the pore space. To date, there are several methods by which these data can be obtained.
One of them is the method of visualization, based on the creation of three-dimensional images by computer processing of the real internal structure of the original samples of the porous medium (or destructive approach by cutting 2D-sections confocal laser scanning microscopy, or nondestructive X-ray microtomography [13-16]) or construction of 3D images from 2D-sections of high resolution using statistical methods or simulation of geological processes. Other non-destructive approaches to date are mercury porometry and gas adsorption, with the help of which it is possible to obtain the distribution of pores in size and surface area within certain assumptions.

Of the existing methods, X-ray microtomography does not allow for the study of nanoporous media, since the maximum resolution of laboratory installations does not exceed 50 nm [17]. The mercury porometry method is the most popular method for characterizing porous materials with pores in the range up to 3 nm [16-18]. Compared to the gas sorption method, it has a much wider range of pores and significantly higher speed. However, the main drawback of the method is the assumption used to represent a porous structure in the form of a bundle of cylindrical pores. When obtaining a pore size distribution, all pores are considered equally available for an external mercury tank. This assumption can only be made if the pore structure is represented by a bundle of capillaries or if the pore connectivity is very high. In fact, however, pore connectivity effects can be very important, leading to dispersion effects when part of the non-wetting liquid can become wetting due to the interaction of adjacent pore clusters [21]. In addition, the method is based on the use of the Laplace equation generalized by Voshburn and the concept of phenomenological wetting angle [22]. At the same time, as numerous studies show, the filling of the disordered nanoporous medium with a non-wetting liquid does not occur according to the Laplace law [21]. Even for a wide distribution of pores by size $\Delta R/R > 1$ the chance to be filled has pores of all radii, and the probability of filling depends on the nearest pore environment. Information about the correlations in the process of filling the non-wetting liquid nanoporous medium and its outflow can lead to the development of a new method of characterization and porous media porosity porometry, which is also one of the most pressing problems in the development, synthesis and use of such media.

In addition, the description of the flow in a porous medium is based on the Darcy equation or the generalized Darcy equation for wetting and non-wetting liquids [23] with boundary conditions of adhesion (for wetting liquids) and boundary conditions of gliding, leading to an increase in the speed of movement in the channel [24-25]. However, recent studies have shown that Darcy’s law may not be fulfilled when liquid is filled with nanoporous media. Thus, modeling the molecular dynamics of water flow through nanoporous media, taking into account different laws of interaction of molecules with the surface of pores, has shown that the permeability can be more than 30 times higher than the results, which were calculated using the Coseni-Karman equation based on the Darcy law. Such an effect can be related both to changes in the flow rate of liquid in a single nanotube and in the case of formation of a percolation cluster medium from the pores grid, the authors unfortunately do not discuss such an interrelation [26]. Due to geometric flow correlations, one can expect changes in the transfer rate of matter in a porous medium [27-30]. It is important to note that in percolating nanoporous media it is possible both to accelerate the transfer rate due to long-range flow correlations in the percolation cluster [27] and to reduce it due to the formation of short-range correlations leading to stagnant zones and a reduction in the number of “transport” pores arising from the configuration of the percolation cluster, which does not ensure equal availability of all its parts.

One of the tasks of characterizing the nanoporous medium is to investigate the properties of the medium, which takes into account both the distribution of pores in size and correlation effects in the mutual arrangement of pores during the flow of liquid through the porous medium. These local configurations interact with each other through an infinite percolation cluster of filled pores in accordance with the mutual arrangement of pores in a frozen random pore structure.
of a porous medium. From the researches carried out for today it follows that disordered environments, usually considered homogeneous, are inherent in such phenomena as heterogeneity and slow relaxation of the formed metastable heterogeneous state, arising due to collective effects in the system of local metastable configurations, which make up the structure of heterogeneous state. If we consider that the disordered nanoporous medium filled with liquid shows the properties typical of the general properties of disordered systems, then the question arises about the reasons for the difference in the nature of relaxation of the state of non-wetting liquid in disordered nanoporous medium from the known general law of relaxation of the properties of disordered systems (glasses). In this connection the problem of characterization of disordered nanoporous media, determination of their structural properties and development of new porous materials by means of investigation of properties at structure manipulation are actual tasks of the present time and underlines the scientific novelty of the work.

Recently, there have been several works that allow us to obtain analytically, within the framework of some assumptions and simplifications, the theoretical dependence of the volume change of the system consisting of nanoporous granules immersed in a non-wetting liquid on the applied pressure (hysteresis) or on time after the removal of the external load (relaxation) [10, 31-33].

The approach proposed in this paper is based on numerical calculations based on the theoretical approaches described in detail in [31-33]. The principal difference from the previously used approaches and novelty lies in the absence of simplifications related to the narrowing of pore size distributions and the number of nearest neighbors, which allows us to take into account in detail the possible geometric configurations, when the pore of the same radius can be surrounded by a different number of neighboring pores. In addition, the use of numerical modeling allows us to obtain a large number of different parameters, ranging from structural characteristics (the number of nearest neighbors, connectivity, etc.), cluster (percolation thresholds) and ending with volume dependencies on pressure and time.

The work structure is as follows. Methodology of modeling, description of numerical experiments in section 2. In section 3 the comparison of the published experimental results and results of numerical modeling on the example of a hysteresis depending on change of volume of system from pressure for porous medium Libersorb23 in water is resulted.

2. Main part

2.1. Modelling procedure

Modelling is carried out in a sequential manner and consists of several steps:

- Generation of porous media
- Infiltration simulation
- Defiltration simulation

The sequence of these steps with fixed medium parameters and maximum filling pressure of $p_{in,max}$ is carried out at least $10^2$ times.

2.2. Generation of porous media

Let’s consider that the filling of porous medium granules occurs independently of each other. This allows us to simulate the filling of a single granule, which is a set of intersecting spheres whose centers lie within the cube with a given size. Behavior of the aggregate of granules is achieved by averaging the results obtained through repeated numerical experiments. The pore space is the space inside the spheres. The porosity of $\varphi$, equal to the ratio of pore volumes in the granule to the cube volume, should be such that the proportion of bound pores significantly exceeds the proportion of pores not belonging to the bound system. For three-dimensional systems the threshold value of porosity varies in the range $\varphi_c = 0.16 \div 0.3$ [34].
Input parameters for the beginning of environment generation are: length of a cube edge $L$, function of distribution of pores on the sizes $f(R)$, porosity $\varphi$, the area of a surface of pores $S_p$, volume of pore space $V_p$. All these parameters, except the cube size, should be taken directly from the experimental material measurements on the corresponding equipment. The cube size should correspond in order of magnitude to the real size of one granule of porous matter. However, as calculations have shown, there is no need to specify such a large size of the system, because starting from several million pores in the simulated granule the results become indistinguishable from each other within the error limits. Besides, if the size of $L$ of porous body granules is much larger than the maximum pore size of $R_{\text{max}}$, then the characteristics of a porous body granule are indistinguishable from the characteristics of an infinite body with the accuracy of $R_{\text{max}}/L \sim 10^{-4} - 10^{-2}$.

Then it is necessary to choose the model of porous media within which the generation will be performed. As a model we used the approach of chaotically arranged spheres of different sizes with a solid core (cherry-pit model). The pore space was the space inside the spheres.

The algorithm is as follows.

1. The maximum value of the pore size distribution function is determined $f(R)_{\text{max}}$.
2. A randomly generated pore size is $R_{\text{gen}}$ within the given distribution ($R_{\text{min}} \leq R_{\text{gen}} \leq R_{\text{max}}$) and a random number $N_{\text{rand}}$ within the range from 0 to $f(R)_{\text{max}}$. If the condition that $f(R_{\text{gen}}) \geq N_{\text{rand}}$ is fulfilled, the pore radius is considered to be generated and the transition to the next step is performed. Otherwise, step 2 is repeated. This simple approach allows us to repeat the experimental distribution function when it does not exist in the analytical form.
3. Coordinates of the future center of sphere $x_{\text{rand}}, y_{\text{rand}}$ and $z_{\text{rand}}$ lying in a range from 0 to $L$, where $L$ — length of a cube edge are generated randomly.
4. The check on intersection of the generated sphere at the previous step with other already existing spheres is carried out. If at least one distance between the centers of spheres will appear less than $\text{core} \ast (R_{\text{gen}} + R_i)$ where index $i$ runs on all spheres the algorithm returns on step 3. The value of $\text{core}$ is responsible for the fraction of the radius that occupies the solid core of the sphere. The case $\text{core} = 1$ corresponds to absolutely non-overlapping spheres which cannot be crossed, and $\text{core} = 0$ — to completely permeable spheres. Thus a choice of value of $\text{core}$ is carried out so that the total specific area of a surface of pores corresponded to experimental value $S_p$.
5. Coordinates $x_{\text{rand}}, y_{\text{rand}}$ and $z_{\text{rand}}$ are saved and the achieved porosity value is checked as $\varphi_{\text{mod}} = 1 - \exp(\sum_i \frac{4\pi R_i^3}{3L^3})$. If it does not exceed the specified number ($\varphi_{\text{mod}} < \varphi$), the whole algorithm is repeated from the second step.

After porosity will reach the set value (from the experimental data), those pores which lie on border of a cube from a simple condition that the distance from the center of sphere to a face of a cube should not be more than radius of sphere are calculated and written down in a array $\text{bound}$. Also for each pore its nearest neighbors from a geometrical condition of intersection of spheres are defined.

2.3. Infiltration simulation

The next step is to simulate the filling of the generated medium with a non-wetting liquid. At the initial point of time the pores in the granule are empty and the liquid pressure is zero. All pores in the $\text{bound}$ array border with non-wetting liquid. Compressibility of porous medium and liquid is neglected. The pressure change is considered to be quasi-static, i.e. $\tau_p > \tau_V \gg \tau_z$, where $\tau_p$ — characteristic time of pressure change, $\tau_V$ — characteristic time of pore filling, $\tau_z$ — characteristic time of barrier-free hydrodynamic pore filling. Such time hierarchy allows to
consider the process of filling of each pore at constant pressure. The sequence of steps to fill an initially empty medium is as follows:

1. The final pressure of $p_{\text{end}}$ and the number of steps on the pressure of $N_p$ are specified, so the step on the pressure is calculated as $p_{\text{step}} = p_{\text{end}}/N_p$.

2. As the first pores which can be filled are the pores lying on a border of a granule at first from an array $\text{bound}$ the pores are chosen randomly in the beginning. If the selected pore is empty, then the work to be spent on filling at the current pressure of $p$ [21] is:

$$\delta A = -pV + (S - S_m) * \delta \sigma + \sigma * (S_e - S_z),$$  

(1)

where $V$ — pore volume, $S$ — internal surface area, $S_m$ — area cut out from the sphere by other spheres intersecting with it, $S_e$ — area of meniscuses which are formed at contact of a current filled pore with neighboring pores, $S_z$ — area of meniscuses which will disappear at pore filling because of contact of two filled pores. $\delta \sigma$ — the difference between the surface energies of the solid–liquid interface and solid–gas interface, $\sigma$ — the surface energy of the liquid.

If the work is negative, the pore is considered filled. The filled pore is added to the $\text{filled}$ array and the flag corresponding to the filling changes its value from 0 to 1.

Then the pore is randomly selected from the $\text{bound}$ array or the nearest neighbor of a random pore from the $\text{filled}$ array. For the chosen pore work also is calculated. If work appears negative, the pore is considered filled up. The filled pore is added in a array $\text{filled}$ and the flag corresponding to filling changes the value from 0 on 1. This step repeats until all pores from a file $\text{bound}$ and the nearest neighbours of pores from a file $\text{filled}$ will be selected. If none of the pores can be filled, the current pressure increases: $p = p + p_{\text{step}}$. Multiple repeats of numerical experiments on filling of porous medium with zero pressure allow to realize various variants of growth of clusters of filled pores.

On each step on pressure there is a array of the filled pores $\text{filled}$ and corresponding volume of the porous environment, which filled with liquid is calculated as the sum of volumes of the filled pores less crossing parts. It allows to plot a dependence of change of volume of simulated system on pressure.

2.4. Defiltration simulation

We will count as the initial state of a porous environment, a state when all pores are filled. The initial pressure can be considered equal to $p_{\text{in max}}$.

Liquid can only flow out of those pores that have a way to flow out. In other words, there must be a continuous chain of other filled pores from the filled pores up to the boundary of the porous medium with the liquid.

The algorithm of defiltration realization is as follows.

1. The number of pressure steps $N_p$ is specified, so the pressure step is calculated as $p_{\text{step}} = p_{\text{in max}}/N_p$.

2. Clusters consisting of filled pores and having an exit on a surface of a cube are defined.

3. The pore belonging to such clusters is selected randomly.

4. The work necessary for the flow out of liquid from pore at the current pressure of $p$ [21] is calculated:

$$\delta A = pV - (S - S_m) * \delta \sigma - \sigma * (S_e - S_z).$$  

(2)

If the work is negative, the pore flow and is removed from the array of filled pores $\text{filled}$ and the algorithm returns to step 2. If it is positive, it will be returned to step 3. Returning to step 2 at the current pressure of $p$ will take place as long as there are filled pores that have an exit to the surface and for which the outflow work is negative. If there are pores that are available
for defiltrate (there is a defiltration path, but the work is positive), then the current pressure
decreases $p = p + p_{\text{step}}$ and then goes to step 2.

Such a sequence makes it possible to obtain the dependence of the volume of the simulated
system at decreasing pressure to zero, i.e. to describe the relaxation of "fast states" in accordance
with [31-33]. The liquid remaining in a porous medium at zero pressure, if there are still clusters
with an exit to the surface, can flow at fluctuation overcoming of the barrier $\delta \varepsilon (R, \theta, T)$. Then
the relaxation time is equal to [31-33]:

$$
\tau = \tau_z \cdot \exp(\delta \varepsilon (R, \theta, T)/T),
$$

(3)

where the barrier is defined as $\delta \varepsilon (R, \theta, T) = -(S - S_m) \cdot \delta \sigma - \sigma \cdot (S_e - S_z)$. From (3) it follows
that the relaxation time of $\tau$ is determined by the waiting time required to overcome the local
barrier and the subsequent barrier–free hydrodynamic time of $\tau_z$ fluid flow. The relaxation of
such "slow states" can also be taken into account within the framework of the proposed model
and the solution of this problem will be done in the next papers.

3. Discussion of results

For the modeling, Libersorb 23 porous medium was chosen, which is filled with non-wetting
liquid — water. The nanoporous medium under study was the commercially available KSK-G
silica gel with a random structure of pores obtained in the solgel process. From [31] parameters
of the Libersorb 23 (L23) porous medium are: density $\rho = 1.7798 \pm 0.0016$ g/cm$^3$, specific
surface area of pores $S = 212 \pm 7$ m$^2$/g, and specific volume of pores $\nu = 0.62 \pm 0.02$ cm$^3$/g.
The pore size distribution appeared to be close to a Gaussian distribution with the mean radius
$\bar{R} = 5.0 \pm 0.2$ nm and the relative FWHM $\delta R/\bar{R} = 0.07$, porosity $\varphi = 0.52$.

![Graph](image_url)

**Figure 1.** Dependence of the fraction of the filled volume of the "Libersorb23 — water" system
on the applied pressure at temperature $T = 281K$

The length of the edge of the simulated cube was $L = 500$ nm, the number of pores in
this cube was determined on the basis of the requirement to achieve the required porosity
and internal specific surface area and was $\sim 2 \cdot 10^5$. We performed 50 cycles: generation of
porous medium, pressure increase (filling), pressure decrease (defiltration). Figure 1 presents
the results of averaging and experimental data from [31]. Compressibility of water, empty frame of porous medium and experimental chamber was subtracted from the data, because the process of modeling does not take them into account. From the figure it is visible that qualitatively and quantitatively it is possible to describe the experimental data.

4. Conclusion

The paper suggests an approach based on the model of chaotically intersecting spheres, where the insides of the spheres play the role of pore emptiness. In this approach, which takes into account the size distribution of pores, the correlation effects in the mutual arrangement of pores during the flow of liquid through the porous medium and the interaction of these local configurations through an infinite percolation cluster of filled pores, it is possible to describe the hysteresis in the infiltration–defiltration of a non-wetting liquid from a disordered nanoporous medium. The proposed approach can be used not only for the analysis of quasi-static filling or abnormally slow relaxation, but also, with some modifications, which would take into account the possibility of simultaneous filling and outflow of liquid from pores, for the analysis of shocks, when there is a rapid increase in pressure and time ratio of $\tau_p > \tau_V \gg \tau_z$ does not apply.

5. Acknowledgements

This work was supported by the Russian Science Foundation (project no. 18-13-00398).

References

[1] Abichou T, Benson C H, Edil T B 2004 Can. Geotech. J. 41 698–712
[2] Aytas S, Yurtlu M, Donat R 2009 J. Hazard. Mater. 172 667–74
[3] Mitrofanova A S and Byrkin V A 2018 J. of Physics: Conf. Ser. 1099 012024
[4] Boult K A, Cowper M M, Heath T G, Sato H, Shibutani T, Yui M 1998 J. Contam. Hydrol. 35 141–50
[5] Ghassemi A, Pak A 2011 Int. J. Numer. Anal. Methods Geomech. 35 886–901
[6] Kohler M, Curtis G P, Kent D B, Davis J A 1996 Water Resour. Res. 32 3539–51
[7] Li S G, Ruan F, McLaughlin D 1992 Water Resour. Res. 28, 2297–306
[8] Ren X, Wang S, Yang S, Li J 2009 J. Radioanal. Nucl. Chem. 283 253–9
[9] Tsai W-F, Chen C-J 1995 J. Eng. Mech. 121 230–243
[10] Bortnikova S A, Belogorlov A A, Borman V D and Tronin V N 2018 J. of Physics: Conf. Ser. 1099 012023
[11] Wang X, Chen C, Zhou X, Tan X, Hu W 2005 Radiochim. Acta 93 273–8
[12] Meakin P, Tartakovsky A M 2009 Rev. Geophys. 47(3)
[13] Huang Y, Yang Z, Ren W, Liu G, Zhang C 2015 Int. J. Solids Struct. 6768 340–52
[14] Christie P, Turberg P, Labiouse V, Meuli R, Parriaux A 2011 Eng. Geol. 117 180–8
[15] Nabawy B S, David C 2016 Geosci. J. 20 1–14
[16] Zeng J H, Feng X, Feng S, Zhang Y C, Qiao J C, Yang Z F 2017 J. Nanosci. Nanotechnol. 17 6459–69
[17] Schlter S, Sheppard A, Brown K, Wildenschild D 2014 Water Resour. Res. 50 3615–39
[18] Giesche H 2006 Part. Part. Syst. Charact. 23 9–19
[19] Leon C A 1998 Adv. Colloid Interf. Sci. 76 341–72
[20] Rouquerol J, et al. 2012 Microporous Mesoporous Mater. 154 2–6
[21] Borman V D, Belogorlov A A, Byrkin V A, Tronin V N 2015 Phys. Rev. E 88 052116
[22] Porcheron F, et. al. 2007 Langmuir 23 3372–80
[23] Derjaguin B V, Churaev N V, Muller V M 1987 Surface Forces (Springer US) 440
[24] Vinogradova O I, Belyaev A V 2011 J. of Phys.: Condensed Matter 23 18
[25] Kheifets L, Neimark A 1987 Multiphase Processes in Porous Media (in Russian) (Moscow: Khimja)
[26] Wang J, Song H, Zhu W, Wang Y, Killough J 2016 Interpretation 5 SB1–SB8
[27] Matveev L B 2016 Abstract of the thesis for the degree of Doctor of Physical and Mathematical Sciences (Moscow)
[28] Dranikov I L, Kondratenko P S, Matveev L B 2004 J. of Exp. and Theor. Phys. 98 945
[29] Dranikov I L, Kondratenko P S, Matveev L B 2004 Izvestia RAN Energetika 4 113–20
[30] Dykhne A M, Kondratenko P S, Matveev L B 2004 JETP Letters 80 410–2
[31] Borman V D, Belogorlov A A, Zharomsckii V M, Tronin V N 2015 J. of Exp. and Theor. Phys. 121 1027–41
[32] Borman V D, Tronin V N 2016 Physica A 457 391–405
[33] Borman V D, Tronin V N, Belogorlov A A 2016 Phys. Rev. E 93 022142
[34] Isichenko M B 1992 Rev. Mod. Phys. 64 961