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A Physics Based Model of Enhanced Gas Production in Mudrocks

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Abstract

Gas flow in mudrocks depends on the complex, multiscale connectivity among nanopores, microfractures and macrofractures. Hydraulic fractures stimulate reservoir volume near a horizontal well and create other fractures at all scales. Elsewhere, we have described the Stimulated Reservoir Volume (SRV) as a fractal with its own fracture network that accesses the organic-rich matrix. In the practically impermeable mudrock, the known volume of fracturing water (and proppant) must create an equal volume of fractures at all scales. Thus, we can constrain the physical structure of SRV, i.e., the number of macrofractures and surface area created after hydrofracturing. Nanopores in the organic matrix act as the source of almost all gas. Here, we present a comprehensive, physics-based microscale model of (a) the increased permeability to gas flow in a mudrock and (b) the effects of smallest nanopores on well production rates and gas storage capacity in this mudrock.

We introduce a physical quantity, the microscale source term, s to study numerically the interactions between microfractures and nanopores. Interactions of this term with the characteristic permeability of multiscale fractures, k_f , defines the productivity and economic viability of gas wells. Most researchers explain enhancements of gas production from shales by invoking slip flow in the nanopores at high Knudsen number, Kn . However, molecular gas dynamics simulations, experimental results in carbon nanotubes, and the calculated Klinkenberg and Browns slippage factors discredit gas slip at high subsurface pressures ($P > 3000$ psi) and with rough pore surfaces. We propose a model of flow of the high-pressure shale gas, and explain the increased permeability in mudrocks without slip flow and Knudsen diffusion. We predict enhanced gas flow at the outlet of a single micropore, caused by an additional gas influx from the numerous nanopores connected to that micropore. We then extend the single micropore model to a network of micropores, each fed by many nanopores. This network idealizes a microfracture network in contact with organic matrix in a mudrock. The overall permeability increase depends on the nanopore radii, flow rate in the microcapillaries, and the persistence of pressure difference between the nanopores and microcapillaries. A no-flow-reversal condition for the micropore network imposes limits on the nanopore radii and pressure differentials along the nanopores.

As the average radius of the nanopores feeding the micropore network increases, the ratio of the volumetric flow rates in the micropores, Q_{out}/Q_{in} , increases faster, because the additional gas influx depends on 4th power of the nanopore radius. An increase of the flow rate into a micropore network reduces the effect of the nanopore influx in the system. Q_{out}/Q_{in} is also highly sensitive to the difference between the pressure in the kerogen and that in the micropores. Isolated nanopores in the organic matrix can feed a micropore for only a few milliseconds, demonstrating that the kerogen matrix has a well-connected nanopore network. A small value of the microscale source term, s , gives additional numerical justification for the concept. The effect of the smallest nanopores with the radii ≤ 1 nm on the gas storage capacity is highlighted. A mere 5% of such nanopores can maintain a long tail of slow production rate from the mudrock reservoirs.

Our analytical solution captures the experimentally observed enhanced flow rate in mudrocks. It presents a numerical justification for a well-connected nanopore network in the organic matrix, and the impact of the smallest nanopores on the long-term production rate from a horizontal well.

Introduction

Gas bearing shales have changed the face of the energy industry in the US and around the world. Shales, playing the role of both source rock and seal, create a multiscale, complex flow system among different components: organic matter, inorganic matter and fractures. Organic matter exists in sheets that are thin compared with the reservoir thickness and stores free and adsorbed gas in nanopores. Adsorbed gas exists because of the intermolecular forces of attraction between the gas molecules and the pore walls, making up to 28% (Etmann *et al.*, 2014) of the total bulk gas present in the system. Highly porous organic matter with the porosity, $\phi_k \approx 20\text{-}40\%$ (Wang *et al.*, 2009; Sondergeld *et al.*, 2010), hosts more than 90% of the bulk porosity (Loucks *et al.*, 2010) and stores most of the gas present in shales, see **Figure 1 (left)**. The average bulk porosity of shales is low, 5-8%, and most of the pores have radii between 2 and 10 nm (Curtis *et al.*, 2010; Nelson, 2009; Loucks *et al.*, 2012a, 2009; Sakhaee-Pour *et al.*, 2012b; Loucks *et al.*, 2012b; Kuila and Prasad, 2013; Sondergeld *et al.*, 2010; Labani *et al.*, 2013; Al Hinai *et al.*, 2014), see **Figure 1 (right)**. Pore size distribution in shales is fractal (Lee *et al.*, 2014; Liu *et al.*, 2015, 2017; Zhang *et al.*, 2014; Zhou and Kang, 2016; Yang *et al.*, 2014; Sun *et al.*, 2017). The minimum pore radius accessed with mercury porosimetry and SEM imaging is 2 nm. However, the low-pressure nitrogen and carbon dioxide gas adsorption reveal pore radii that are less than 1 nm, and make up to 5-15% (Chalmers *et al.*, 2012; Labani *et al.*, 2013; Al Hinai *et al.*, 2014; Tian *et al.*, 2013b) of all pores. At high subsurface pressure and small nanopore volume, gas molecules in the nanopores are densely packed and may exist in the supercritical state, (Patzek, 2017). The average gas density increases (see **Figure B1 (left)**; (Dombrowski *et al.*, 2000; Mohammad *et al.*, 2009; Zhou and Wang, 2000; Soule *et al.*, 2001; Didar *et al.*, 2013)), and the gas confinement also causes radial viscosity variation, see **Figure B1 (right)**, (Sheng *et al.*, 1989; Ihm *et al.*, 1991; Mehdipour and Eslami, 2002; Derouane *et al.*, 1987). The high average density of gas in these smallest nanopores packs a significant amount of gas in the source rock. These packed gas molecules help in maintaining a small production rate for many years.

Permeability of an unstimulated source rock is very small, 5 – 10 nD, because of the small cross-sectional areas of pore throats. Economic production starts only after hydrofracturing that creates a new complex fracture system in the source rock. Natural fractures reactivated during hy-

drofracturing expose organic matrix nanopores to the highly permeable channels, thus increasing effective permeability of the source rock. However, the limited permeability enhancement measured by the flow experiments in cores, cannot explain the high production rate in mudrocks. For the nanopore radii in the range of 2-10 nm, slip-flow and Knudsen flow based on *Tsien* (1946) flow regime are invoked to explain the increased flow rate (*Ertekin et al.*, 1986; *Javadpour et al.*, 2007, 2009; *Civan*, 2010). For such small pores, the mean free path of molecules is comparable with the length scale of the system, the Knudsen Number (Kn) is more than 1, the continuum approximation breaks, and the molecules slip because of collisions with the pore wall. However, justifying

Figure 1: Left: SEM image of a kerogen body showing porosity. The kerogen hosts more than 90% of the pores in shales and stores almost all hydrocarbons. The porosity of the kerogen enclosed by the red boundary is 48 to 55 %. Source: *Sondergeld et al.* (2010). **Right:** Pore size distribution from the SEM image of a shale sample. The dominant pore radius between 2-5 nm accounts for more than 80% of the total pores present in the organic matrix. Large pores ($r > 5$ nm) account for 10% and are the potential crack areas during hydrofracturing. Sudden gas release from these large pores is responsible for initial high production rate for the first few months. Adapted from *Curtis et al.* (2010).

slip flow in nanopores based on high Knudsen number is misleading, as the underlying theory was developed for rarefied gases at high altitudes and low pressure. Transport of high pressure gases in shales (1000's of psi) does not follow this theory. *Roy et al.* (2003) showed only a 4-8 % increase in gas flow rates, because of the slip in carbon nanotubes. *Sakhaee-Pour et al.* (2012a); *Jin and Firoozabadi* (2015); *Wasaki et al.* (2015); *Villazon et al.* (2011); *Islam and Patzek* (2014) showed negligible effect of slip flow even for the smallest nanopores at high subsurface pressure >5000 psi. *Patzek* (2017) highlighted the disappearance of slip flow at the pressures above 150 psi, and suggested that Knudsen scaling does not apply to gas shales.

Surface diffusion of gas adsorbed has been proposed as a possible mechanism of permeability enhancement. However, recently reported experimental values of the diffusion coefficient (*Wang et al.*, 2016; *Chen et al.*, 2018; *Wang et al.*, 2017) are too low, $10^{-9} - 10^{-10}$ m²/s for surface diffusion and $10^{-16} - 10^{-19}$ m²/s for solid kerogen diffusion. With the above-reported values, **Figure 2 (left)** shows the effect of the diffusion coefficient on the surface diffusion ratio in the mudrock operational regime. The surface diffusion ratio, see Appendix C, is defined as the flow contribution from surface diffusion of adsorbed gas in a nanopore/total flow in a nanopore. The effect is negligible for a wide range of gas pressures (2000-8000 psi).

When the supernatural explanations of the enhancement of flow properties of shales are abandoned, one needs to take a careful look at the SEM images of shale samples. The FIB-SEM images from *Chalmers et al.* (2012); *Curtis et al.* (2012); *Cardott et al.* (2015); *Slatt and O'Brien* (2011b); *Chen et al.* (2015); *Li et al.* (2013) and core samples highlight the multiscale connectivity (*Tahmasebi et al.*, 2016; *Landry et al.*, 2014; *Gale et al.*, 2007; *Chen et al.*, 2015) in mudrocks. At the microscale, the disconnected organic matter patches exist, each having its own well-connected network of nanopores (*Tian et al.*, 2013a; *Slatt and O'Brien*, 2011a; *Huang et al.*, 2013; *Sondergeld et al.*, 2010; *Curtis et al.*, 2010). In an unstimulated source rock, the lack of connectivity between these independent patches of well-connected nanopores makes economic gas production impossible. After stimulation, fractures induced at the macroscale, and the reactivated natural fractures connect the otherwise disconnected organic matter patches by exposing the locally connected nanopores to the highly permeable channels. Huge surface area of the order of 10^5 - 10^6 m² (*Johri and Zoback*, 2013; *O'Malley et al.*, 2016) created during hydrofracturing is responsible for the effective connection between the micro- and macroscale (*Li et al.*, 2013; *Ougier-Simonin et al.*, 2016). At the reservoir scale, the discrete fracture network created by hydrofracturing further connects the macroscale fractures. *Raterman et al.* (2017) showed permeability enhancement through the frequent occurrence of such discrete fractures in the Eagle Ford core samples. Thus, the hierarchical network of nanopores → microfractures → macrofractures → discrete fracture network, all connected in the increasing order of their sizes, create a multiscale system effectively draining gas from the nanopores to the wellbore, see **Figure 2 (right)**.

Figure 2: Left: Surface diffusion ratio shows the contribution of surface diffusion to total flow through a nanopore. For subsurface gas pressures between 2000-5000 psi, the surface diffusion contribution in a nanopore of radius 1 nm is negligible for $D_s = 10^{-9}$ m²/s. **Right:** SEM images of shale samples. In SEM(a) and SEM(b) the grey part is the organic matrix and the lighter part is the inorganic matrix. SEM(c) and SEM(d) shows microfractures created during hydrofracturing, which connects the otherwise disconnected organic matter. Organic matter nanopores exposed by microfractures discharge gas into the macroscale fracture network and maintain production. Source: *Chalmers et al.* (2012), *Cardott et al.* (2015).

Haider et al. (2020) used fractal theory to describe multiscale connectivity in a Stimulated Reservoir Volume (SRV). The physical properties of a fractal SRV, i.e., (a) fracture permeability (k_f), (b) fracture porosity (ϕ_f), and (c) microscale source term s , are maximum at the hydrofracture

face, see **Figure 3 (left)**. Further away from the hydrofracture face, the values of k_f , ϕ_f , and s decrease following a power law. k_f quantifies the permeability increase at the macroscale because of the induced large scale fractures, and s quantifies the connection between nanopores embedded in the organic matrix and the reactivated natural fractures. **Figure 3 (right)** shows the values of s at the hydrofracture faces of 30 Barnett wells (Haider *et al.*, 2020). These values were obtained by numerical fitting of the well production data with an optimization function. Higher values of s imply better exposure of organic nanopores to the highly permeable microcracks. The network of nanopores and natural fractures, which is further connected to macrocracks, creates a multiscale system responsible for the high production rate in mudrocks.

Figure 3: Left: Fractal reservoir volume after hydrofracking. Source: Haider *et al.* (2020). Right: Microscale source term, s , for the simulated wells are limited by the maximum depicted as the continuous line at the fracture face. A low value of s from the simulation means that only a small part of the stimulated surface is connected well enough for efficient gas production. Source: Haider *et al.* (2020)

Table 1: Model parameters

Q_{in} :	Inlet flow rate (500-1250 μm^3)	dx :	Distance between nanopores
Q_{out} :	Outlet flow rate	r :	Nanopores radius (5-25 nm)
P_m :	Pressure in nanopore (2000-5000 psi)	P_i :	Capillary inlet pressure
P :	Pressure in capillary	x :	Distance along the capillary
l :	Nanopore length (60 μm)	L :	Capillary length (4000 μm)
R :	Capillary radius (4 μm)	μ :	Viscosity

In this paper, we present a quantitative model of microscale permeability increase in a stimulated matrix, resulting from better communication and gas discharge between nanopores and microcracks. We represent the high permeability system as a capillary or a network of capillaries that are being fed by gas from the nanopores connected to its surface, see **Figs. 7 and 9**. Pressure difference between the microcrack and the nanopore facilitates gas discharge. The radius and length of the nanopore feeding the network are described as r and l . The radius and length of the capillary are R and L , respectively. In the subsurface, a network of capillaries represents a system of connected microfractures in contact with the organic matrix having a locally well-connected nanopore network. The initial flow rate in the network is given by Q_{in} , and the flow rate, Q_{out} , at the outlet of this network increases because of the efficient gas discharge from the connected nanopores. The Results and Discussion section shows how the connected network increases flow

rate and parameters that control the flow. The parameters that control the increased flow rate in the network are, (a) radii of the nanopores, (b) the number of nanopores feeding the network, and (c) the initial flow rate, Q_{in} , in the network. The effect on large nanopores (radii > 5 nm) on the increased flow rate in a capillary or a network of capillaries is quantified by Q_{out}/Q_{in} . The idea of a well-connected network of smaller nanopores (radii < 5 nm) acting as a continuous background source of gas for larger nanopores, thus creating a multiscale system, is investigated numerically. We also highlight the importance of nanopores less than 1 nm in radius in terms of the storage capacity and production profile of a shale well.

Results and Discussion

Flow rate in a capillary and a network of capillaries: For a microcapillary and a network of microcapillaries, the ratio of Q_{out}/Q_{in} depends on three variables, (a) the average radius, r , of the nanopores that discharge gas into the capillaries; (b) the inlet flow rate, Q_{in} , in a capillary/network of capillaries; and (c) the pressure difference, $P_m - P_{in}$, between the capillary and nanopores, see **Figure 4 (left)**. For a microcapillary, the ratio of Q_{out}/Q_{in} increases from 1.1 to 3.77 ($Q_{in} = 753 \mu\text{m}^3/\text{s}$) as the nanopore radius increases from 5 nm to 25 nm. The ratio Q_{out}/Q_{in} increases faster for larger radii, because gas flow in the nanopores follows the Hagen-Poiseuille law that depends on the 4th power of the nanopore radii. The higher inlet flow rate in the capillary suppresses the relative contribution of the nanopore discharge, making the curve shift downwards. The network of capillaries shows similar behavior. **Figure 4 (right)** shows the effect of number of nanopores feeding the microcapillary on Q_{out}/Q_{in} . The percentage of microcapillary surface area in contact with the nanopores, presented here as the Surface coverage, quantifies the number of nanopores feeding the microcapillary. A higher fractional of coverage of the surface means a larger number of nanopores feeding the microcapillary. For the surface coverage between 10-20%, additional gas influx into the microcapillary is negligible for a wide range of nanopore radii (5-20 nm).

For the surface coverage $> 30\%$, the flow-enhancement is quite pronounced for the nanopore radii in the range of 5-15 nm that corresponds to the dominant pore radius in a kerogen pore network. This shows that for gas flow in shales with higher production rate, most of the nanopores must be connected to the fracture network which act as highly permeable pathways and maintain high production rate.

Effect of disconnected nanopores: SEM images show that the organic matrix hosts most of the nanopores. Nanopores exposed to the microfracture network after simulation create the highly permeable pathways to sustain long term production. The model presented here considers nanopores connected to the capillary network as closed bottles, meaning they are not connected to a continuous supply of gas from the kerogen. In that case, it will take only a few milliseconds for the nanopore gas to discharge into a microcapillary before pressure equilibrium is reached and the flow stops. The initial high ratio of Q_{out}/Q_{in} is sustained only for a short time and then it drops to 1, see **Figure 5 (left)**. As the initial inlet flow rate in the capillary increases, the time required to reach $Q_{out}/Q_{in} = 1$ also increases, because the nanopores discharge more slowly. So, to maintain a continuous supply of gas in the microcapillary, the nanopores must be locally well connected to the smaller nanopores in the bulk kerogen. This connectivity maintains the continuous supply of gas from the kerogen to the microcracks. **Figure 5 (right)** gives a numerical justification of the

Figure 4: Left: Ratio of Q_{out}/Q_{in} for a single capillary. Nanopores connected to the capillary surface contribute to $Q_{out} > Q_{in}$. For a fixed inlet flow rate, Q_{in} in the capillary, the ratio Q_{out}/Q_{in} increases with nanopore radius. For larger nanopore radii, the effect is more pronounced, because the contribution from a nanopore depends on the 4th power of its radius following the Hagen-Poiseuille law. At higher inlet flow rates, the ratio Q_{out}/Q_{in} decreases. **Right:** Ratio of Q_{out}/Q_{in} for a capillary network. A higher fraction of the capillary surface covered with nanopores causes more discharge and increases the ratio Q_{out}/Q_{in} . The effect is minimal for the surface coverage of 10%. This highlights the importance of microfractures exposing nanopores to the highly permeable pathways. The variables affecting the ratio Q_{out}/Q_{in} are the nanopore radius; the inlet flow rate, Q_{in} , in the capillary; and the pressure difference between the nanopores and the capillary.

Figure 5: Left: The disconnected nanopores of 10 nm radius act as bottles that discharge gas into the capillary within a few milliseconds and reach equilibrium. The high value of Q_{out}/Q_{in} is sustained for a short time. At a higher inlet flow rate, Q_{in} , the equilibrium time is slightly prolonged because of the relatively slower discharge from the nanopores. To sustain long-term production, these nanopores must be locally well-connected within the kerogen specks seen in the SEM images. **Right:** The nanopores with radii > 5 nm are effective in discharging gas into the capillary, thus increasing the total flow rate in the system. Small pores with radii < 5 nm do not have a significant contribution to flow.

idea of a locally well-connected nanopore network. Large nanopores (radii > 5 nm) are effective in draining gas into the capillary network and increasing flow rate of the system, compared with the smaller nanopores (with radii < 5 nm). Nanopores with the radii < 5 nm do not increase gas flow rate, and do not increase the overall permeability of the source rock. Additionally, experimental and numerical results show the creation of the highly permeable channels close to larger nanopores

(Berthonneau *et al.*, 2018). Thus, the small nanopores must be connected to the larger nanopores as the continuous gas feeders, creating a multiscale network of pores and microcracks that together sustain long-term production from a horizontal gas well.

Effect of smallest nanopores: **Figure B1** shows the radial density and viscosity profiles of methane gas in a cylindrical nanopore. The methane density in pores with $r < 1$ nm is 4 times higher than its bulk density. Average density of gas increases sharply in the pores with radii less than 1 nm. The ordered methane viscosity can be 5 times higher than its bulk viscosity. A small volumetric fraction of these tiny nanopores can store a significant amount of gas. For example, **Figure 6 (right)** shows the production rates from 20 horizontal, hydrofractured Barnett shale wells. Most Barnett wells might produce (Patzek *et al.*, 2013, 2014, 2019) in excess of 2×10^{25} methane molecules per second for 2-3 years. We assume that the average wellbore lateral length and hydrofracture height are 1000 m and 30 m, respectively. If the pores in the source rock are assumed to be cylinders with the radius $r = 5$ nm and length $3r$, then the dense hexagonal packing of methane molecules in the pores would require the width of the bulk rock parallelepiped (average tip-to-tip hydrofracture length) to be 165m. Therefore, the bulk rock volume required to produced the gas would be 5 Mm^3 . In 3 years, assuming a recovery factor of 0.3, the actual bulk rock volume required to pro-

Figure 6: Left: Production rate from horizontal wells in the Barnett shale. A decent well might produce 2×10^{25} methane molecules per second for 2-3 years. **Right:** With 8% porosity, the rock volume required to store gas as densely packed molecules in 100% of the pores is 5 Mm^3 compared to 13.7 Mm^3 for a normal well. Dense packing of molecules in the nanopores with diameter < 2 nm, and the average gas density $1.5 \times$ bulk density, requires 15% of these pores by volume to sustain well production for 2 years at the maximum production rate. 5-10 % of these pores, with a high average gas viscosity, causes the slow, continuous discharge of molecules that maintains the multi-year tail in the late stage of a well's life.

duce the gas would be 13.5 Mm^3 , see **Figure 6 (right)**. In 13.5 Mm^3 of bulk rock, if we assume that pores with $r < 1$ nm have an average gas density of $1.5 \times$ bulk density, then only 15% of these pores can maintain the production for 3 years at the highest initial rates of production. The production rate of a well after 2-3 years is 4-5 times less than the initial production rate. In later years on production, a shale gas well has the $4 - 5 \times$ lower production rate that can easily be sustained by these small nanopores for 5-10 years. In summary, the high viscosity of gas in the small nanopores that slows down the production rate, and the high gas density in these nanopores can be effective in maintaining the late-stage production from the well.

Materials and Methods

Single Capillary Model: A microfracture in contact with the organic matter is idealized as a capillary with an opening on its surface for gas transfer from the organic nanopores. Elsewhere in the paper, organic matter having nanopores filled with gas is termed “kerogen”. **Figure 7 (left)**, shows a microcapillary in contact with the equally-spaced kerogen nanopores along its length. P_{in} and Q_{in} are the inlet pressure and inlet flow rate in the microcapillary, respectively. P_{out} and Q_{out} are the pressure and flow rate at the end of the microcapillary. The pressure outside the capillary is constant and is equal to the kerogen pressure P_m in the nanopores. The nanopores are separated by

Figure 7: Left: A microcapillary of radius R and length L fed by additional gas influx from nanopores connected to its outer surface. Q_{in} is the inlet flow rate in the capillary. Additional nanopore gas influx makes $Q_{out} > Q_{in}$. In the subsurface, this microcapillary represents a fracture and the nanopores on the capillary surface represent the exposed kerogen speck with the locally well-connected nanopores. **Right:** The unwrapped capillary with the black dots as the projection of the nanopores connected to its outer surface.

Figure 8: Model Development: Moving from x to $x + dx$, the gas pressure and flow rate change to $P(x + dx)$ and $Q(x + dx)$, respectively. Pressure decreases in the flow direction with the gradient dP/dx . The gas influx from the nanopores at $x + dx$ is responsible for increasing the overall flow rate.

a fixed distance and feed gas into the capillary only at the specified points. The pressure difference between the nanopores and the capillary feeds the capillary with additional gas flux, making $Q_{out} > Q_{in}$. The unwrapped schematic diagram in **Figure 7 (right)** of the microcapillary shows the projection of the connected nanopores as black dots, where L and R corresponds to the length and radius of the capillary. **Figure 8** presents the schematic view of the model development. The mathematical development of the model is similar to fluid flow in permeable tubes and renal tubes (Karode, 2001b,a; Davis, 1978; Marshall and Trowbridge, 1974; Ku and Leidenfrost, 1981; Damak et al., 2004). At a distance x , the pressure and flow rate in the microcapillary are $P(x)$ and $Q(x)$. At an incremental distance dx , the pressure and flow rate are $Q(x + dx)$ and $P(x + dx)$, following the pressure gradient dP/dx . Moving from x to $x + dx$, increases the flow rate i.e., $Q(x + dx) > Q(x)$, because of gas influx from the nanopores at $x + dx$.

Considering Hagen-Poiseuille flow in a circular capillary, the pressure gradient and flow rate at point x is:

$$\frac{dP(x)}{dx} = -\frac{8\mu Q(x)}{\pi R^4} \quad (1)$$

Differentiating eq. (1), gives the change of flow rate per unit x as we move from x to $x + dx$:

$$\frac{d^2 P(x)}{dx^2} = -\frac{8\mu}{\pi R^4} \frac{dQ(x)}{dx}$$

$$\frac{dQ(x)}{dx} = -\frac{d^2 P(x)}{dx^2} \left(\frac{\pi R^4}{8\mu} \right) \quad (2)$$

The flow rate gradient depends on the additional gas influx from nanopores as we move from distance x to $x + dx$. Assuming that nanopores cover 30 percent of the microcapillary circumference, additional influx at x to $x + dx$ will be equal to the influx from the nanopore at $x + dx$ which is given by:

$$\Delta Q(x + dx) = \frac{\pi r^4}{8\mu} \frac{\left\{ P_m - \left(P(x) + \frac{dP}{dx} \Delta x \right) \right\}}{l} \times 0.3 \frac{2\pi R}{2r} \quad (3)$$

where P_m is the pressure in the nanopore and $P(x) + \frac{dP}{dx} dx$ is pressure in the microcapillary at $x + dx$. The factor $(0.3 \times 2\pi R / 2r)$ takes into account the fact that only 30% of the capillary circumference is covered by the nanopores. The flow gradient using eq. (3) is given by:

$$\frac{\Delta Q}{\Delta x} = \frac{dQ}{dx} = 0.3 \frac{\pi^2 r^3 R}{8\mu} \frac{\left\{ \frac{P_m - P(x)}{\Delta x} - \frac{dP}{dx} \right\}}{l} \quad (4)$$

Substituting eq. (4) into eq. (2), the pressure drop along the capillary length is given by:

$$\frac{d^2 P}{dx^2} = 0.3 \frac{\pi r^3}{R^3 l} \left\{ \frac{P(x) - P_m}{\Delta x} + \frac{dP}{dx} \right\} \quad (5)$$

eq. (5), is an ordinary differential equation of the form: $Y'' + aY' + bY = g(x)$ that can be solved after setting the boundary conditions:

$$\text{Boundary Conditions : } \begin{cases} x = 0, P = P_{in} \\ x = l, \frac{dP}{dx} = -Q_{in} \frac{8\mu}{\pi R^4} \end{cases} \quad (6)$$

The final analytical solution for the pressure drop in the capillary because of gas influx from the nanopores is given by:

$$P(x) = \frac{P_{in} - P_m}{\lambda_1 - \lambda_2} \left\{ \lambda_1 e^{\lambda_2 x} - \lambda_2 e^{\lambda_1 x} \right\} + \frac{8\mu Q_i}{\pi R^4 (\lambda_1 - \lambda_2)} \left\{ e^{\lambda_2 x} - e^{\lambda_1 x} \right\} + P_m \quad (7)$$

where

$$\lambda_1 = \frac{c_1 + \sqrt{c_1^2 + 4c_2}}{2}; \lambda_2 = \frac{c_1 - \sqrt{c_1^2 + 4c_2}}{2}; c_1 = \frac{0.3\pi r^3}{R^3 l}; c_2 = \frac{c_1}{\Delta x} \quad (8)$$

Capillary network model: The solution for a capillary model is applied to a 2D network of 12 capillaries, see **Figure 9**. The grey region is the organic matrix having thousands of embedded nanopores. The microcapillaries are 4000 μm long, and their radii vary from 1 to 4 μm . The nanopores in the organic matrix feed gas into the microcapillaries. The inlet and outlet pressures are defined as P_{in} and P_{out} , with the no-flow boundary condition at the top and bottom of the network. Increase in the total outflow, because of the gas influx from the nanopores to the capillaries, is calculated with the following assumptions:

- (a) The nanopores are uniformly distributed in the matrix and the number of nanopores feeding all the capillaries is same
- (b) The pressure in the matrix is fixed in the whole domain and is equal to the inlet pressure to the nanopores, P_m , as in the case of a single capillary
- (c) The additional pressure decrease in each capillary, because of the influx from the nanopores, is proportional to the initial pressure decrease in the capillaries without the effect of nanopores.

With the three assumptions above, the capillary network model is solved as follows:

Step 1: The capillary network is solved without influx from nanopores to get the flow direction in the microcapillaries using a simple mass balance and Hagen-Poiseuille equation with the following boundary conditions.

$$\text{Boundary Conditions : } \begin{cases} x = 0, P = P_{in} \\ x = L, P = P_{out} \end{cases} \quad (9)$$

where L is the microcapillary length equal to 4000 μm , and P_{in}, P_{out} are the inlet and outlet pressures in the network. Solving the network gives pressure at all the network nodes.

Step 2: Because of the assumption c, the flow direction in the microcapillaries remains the same after the introduction of nanopores. With the known flow direction, we use the single capillary model equations and apply mass conservation to all nodes of the network to obtain Q_{out} . Solving eq. (5) with the boundary conditions in eq. (9), gives the analytical solution for flow in each capillary in the capillary network:

$$P(x) = \frac{P_m - P_{out}}{e^{\lambda_1 L} - e^{\lambda_2 L}} \left\{ e^{\lambda_2 x} - e^{\lambda_1 x} \right\} - \frac{P_m - P_{in}}{e^{\lambda_1 L} - e^{\lambda_2 L}} \left\{ e^{\lambda_1 L} e^{\lambda_2 x} - e^{\lambda_2 L} e^{\lambda_1 x} \right\} + P_m \quad (10)$$

where λ_1 and λ_2 are defined as in the single capillary case. Differentiating eq. (10) gives the pressure gradient in each capillary along its length and the flow rate at any point x along the capillary using the Hagen-Poiseuille equation:

$$\frac{dP(x)}{dx} = \frac{P_m - P_{out}}{\lambda_2 e^{\lambda_1 L} - \lambda_1 e^{\lambda_2 L}} \left\{ e^{\lambda_2 x} - e^{\lambda_1 x} \right\} - \frac{P_m - P_{in}}{e^{\lambda_1 L} - e^{\lambda_2 L}} \left\{ \lambda_2 e^{\lambda_1 L} e^{\lambda_2 x} - \lambda_1 e^{\lambda_2 L} e^{\lambda_1 x} \right\} + P_m \quad (11)$$

Step 3: With the known flow direction and nodal pressures in the network, mass balance is applied at all the nodes using eqs. (10) and (11) to get the contribution from the nanopores feeding the capillary up until flow reversal happens in the network and loss of stability.

Figure 9: Left: Idealized subsurface fracture network in contact with the organic matrix containing thousands of nanopores. The black cubes represent the matrix containing nanopores. The vertical and horizontal lines represent microfractures. The locally connected nanopores present in the organic matrix are exposed to the highly permeable fracture network. This multiscale network explains the high production rate in mudrocks (shales) without introducing slip flow or Knudsen diffusion. **Right:** The fracture network is represented as a network of capillaries and the organic matrix. The outflow from the capillary network increases because of gas influx from the nanopores.

Flow reversal in a microcapillary: If the nanopore radius is very large in a microcapillary, the high discharge rate from the nanopores reverses the original predefined flow direction in the microcapillary. Thus, applying the “no flow reversal” condition helps in limiting the maximum radius of the nanopores. Additionally, flow reversal depends on the value of the initial flow rate, Q_{in} , and the pressure difference, $P_m - P_{in}$. The maximum limiting value of the nanopore radius is found by analyzing the flow at the minimum possible Q_{in} , and the maximum possible value of $P_m - P_{in}$, because then we establish the maximum influence of nanopores. Flow reversal problem in the network of microcapillaries is handled similarly.

Conclusions

We have simulated the increase of gas flow rate at the outlet of a capillary/capillary network, caused by the additional gas influx from the nanopores connected to the network’s outer surface, and present the following conclusions:

- The contribution of surface diffusion of adsorbed gas to the total flow in a nanopore is negligible at the experimentally reported values of the diffusion coefficient. Slip flow is also negligible at the high subsurface pressures in shales.
- Hydrofracturing reactivates natural fractures and creates a large surface area that exposes the nanopores in the organic matter to the highly permeable pathways. Microfractures bridge the disconnected nanopore clusters and create multiscale connectivity.
- The nanopores in contact with the multiscale fracture network effectively discharge gas, and increase gas production rate in mudrocks (shales). There is no need to introduce the special effects of slip flow and Knudsen diffusion.

- A small fraction ($< 20\%$) of the nanopores connected to the surface of a capillary has a small effect on the increased flow rate in the capillary, see **Figure 4 (right)**. Therefore, a relatively large fraction of the nanopores must communicate with the microcracks in order to increase the overall rock permeability. This pressure and flow communication is achieved through the huge fractal surface area created during hydrofracturing.
- The disconnected nanopores discharge gas in few microseconds before equilibration. Therefore, these nanopores must be locally well connected to maintain pressure support and continuous gas discharge from the kerogen to the microfractures.
- Only large nanopores (with radii > 5 nm) in contact with the microcracks can increase the permeability of the source rock, see **Figure 5 (right)**. The small nanopores (with radii < 5 nm) act as gas feeders for the larger nanopores and create a locally well-connected network.
- The nanopores less than 1 nm in radius have a significant effect on gas storage capacity in the rock and on long-term production. The pores with $r < 1$ nm, and average gas density $1.5 \times$ bulk density of methane store 50% more gas. 15% by volume of these nanopores can keep a well producing at the highest production rate for 2-3 years. The high gas density and viscosity in these nanopores could be responsible for the long tail in the production of shale wells.

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Nomenclature

Parameters

μ	Viscosity [kg/m.s]
ρ	Density [gm/cm ³]
L	Microcapillary length [m]
l	Nanopore length [m]
P	Pressure [Pa]
Q	Flow rate [m ³ /s]
x	Distance [m]

Subscripts

in	Inlet
m	Nanopore
out	Outlet

Appendix A: Density Functional Theory

Rangarajan *et al.* (1995) developed the *Simplified Local Density* (SLD) model for a slit, using mean-field approximation of the general density functional theory. At equilibrium, the molar chemical potential is given by the sum of fluid-fluid and fluid-solid interactions as:

$$\mu(z) = \mu_{\text{bulk}} = \mu_{\text{ff}}(z) + \mu_{\text{fs}}(z) \quad (\text{A1})$$

where the subscripts “bulk”, “ff”, and “fs” refer to the bulk, fluid-fluid and fluid-solid chemical potentials, respectively and z refers to the distance from the adsorbent surface. Using slit geometry with molecules in between two planes, eq. (A1) is given by:

$$\mu(z) = \mu_{\text{bulk}} = \mu_{\text{ff}}(z) + \mu_{\text{fs1}}(z) + \mu_{\text{fs2}}(W - z) \quad (\text{A2})$$

where W is the slit width and z or $W - z$ refer to the position of the molecules from relative to either of the two surfaces of the slit. The chemical potential of the bulk fluid is given in terms of the fugacity:

$$\mu_{\text{bulk}} = \mu_0(T) + RT \ln \left(\frac{f_{\text{bulk}}}{f_0} \right) \quad (\text{A3})$$

where f_{bulk} is the bulk fugacity and f_0 is the fugacity at a reference state. Similarly, the chemical potential of the molecules due to the fluid-fluid interactions is given by:

$$\mu_{\text{ff}} = \mu_0(T) + RT \ln \left(\frac{f_{\text{ff}}(z)}{f_0} \right) \quad (\text{A4})$$

where $f_{\text{bulk}}(z)$ is the fluid fugacity and f_0 is the fugacity at a reference state. For a parallel plane slit, the fluid-solid chemical potential is given by:

$$\mu_{\text{fs}} = N_A [\Psi^{\text{fs}}(z) + \Psi^{\text{fs}}(W - z)] \quad (\text{A5})$$

where N_A is Avogadro number and $\Psi^{\text{fs}}(z)$ and $\Psi^{\text{fs}}(W - z)$ are the fluid-solid interactions from the two surfaces of a slit of the width W .

Substituting eqs. (A2) and (A4) into eq. (A1), we get the equilibrium criteria for adsorption within a slit given by the equation:

$$f_{\text{ff}}(z) = f_{\text{bulk}} \exp \left(- \frac{\Psi^{\text{fs}}(z) + \Psi^{\text{fs}}(W - z)}{kT} \right) \quad (\text{A6})$$

where k is the Boltzmann constant and T is the absolute temperature. *Chen et al.* (1997) gave the following equation for the interaction potential between a solid and fluid

$$\Psi^{\text{fs}}(z) = 4\pi\rho_{\text{atoms}}\sigma_{\text{fs}}^2 \left(\frac{\sigma_{\text{fs}}^{10}}{5(z')^{10}} - \frac{1}{2} \sum_{i=1}^4 \frac{\sigma_{\text{fs}}^4}{(z' + (i-1)\sigma_{\text{ss}}^4)} \right) \quad (\text{A7})$$

where ϵ_{fs} is the fluid-solid interaction energy parameter, ϵ_{ss} is the solid-solid interaction energy, $\rho_{\text{atoms}} = 0.382 \text{ atoms/\AA}^2$ is the carbon atom density, and σ_{ff} and σ_{ss} are the diameters of methane molecules and the carbon interplanar distance, respectively. The carbon interplanar distance was taken to be that of graphite, 0.335 nm. The Peng-Robinson EOS is coupled with the SLD model to calculate gas fugacity:

$$\frac{P}{\rho RT} = \frac{1}{1 - \rho b} - \frac{a(T)\rho}{RT[1 + (1 - \sqrt{2}\rho b)][1 + (1 + \sqrt{2}\rho b)]} \quad (\text{A8})$$

$$a(T) = \frac{0.45753\alpha(T)R^2T_c^2}{P_c} \quad (\text{A9})$$

$$b = \frac{0.077796RT_c}{P_c} \quad (\text{A10})$$

The bulk fugacity in terms of bulk fluid density is given by:

$$\begin{aligned} \ln \frac{f_{\text{bulk}}}{P} &= \frac{b\rho}{1 - b\rho} - \frac{a(T)\rho}{RT(1 + 2b\rho - b^2\rho^2)} - \\ \ln \left[\frac{P}{RT\rho - \frac{Pb}{RT}} \right] &- \frac{a(T)}{2\sqrt{2}bRT} \ln \left[\frac{1 + (1 + \sqrt{2})\rho b}{1 + (1 - \sqrt{2})\rho b} \right] \end{aligned} \quad (\text{A11})$$

where P is the bulk fluid pressure, ρ is the bulk density, and a and b are the EOS constants given by the eqs. (A10) and (A11)

Similarly, the fugacity of the fluid-fluid interactions is given by:

$$\begin{aligned} \ln \frac{f_{\text{ff}}(z)}{P} &= \frac{b\rho(z)}{1 - b\rho(z)} - \frac{a_{\text{ads}}(z)\rho(z)}{RT(1 + 2b\rho(z) - b^2\rho^2(z))} - \\ \ln \left[\frac{P}{RT\rho(z) - \frac{Pb}{RT}} \right] &- \frac{a_{\text{ads}}(z)}{2\sqrt{2}bRT} \ln \left[\frac{1 + (1 + \sqrt{2})\rho(z)b}{1 + (1 - \sqrt{2})\rho(z)b} \right] \end{aligned} \quad (\text{A12})$$

where the attractive term a_{ads} is a function of position in the slit and, therefore accounts for the fluid-fluid interactions in the slit. *Chen et al.* (1997) developed the equations for $a_{\text{ads}}(z)$, which depend on the ratio of slit width L to the molecular diameter σ_{ff} .

Appendix B: Chapman-Enskog Theory

For a dense gas that consists of rigid spherical molecules, the expression for the viscosity coefficient is given by:

$$\mu = \frac{\mu_0}{\chi} \left[1 + \frac{4}{5}b\rho\chi + 0.761(b\rho\chi)^2 \right] \quad (\text{B1})$$

where μ_0 is the dilute gas viscosity, ρ is the molar density, $b = 2\pi N_A \sigma^3/3$, σ is the molecular diameter, N_A is the Avogadro number, and χ is the value of equilibrium radial distribution function at a distance σ from the center of an individual molecule.

For a hard sphere system, the value of μ_0 and χ is given by:

$$\mu_0 = 1.016 \times \frac{5}{16} \frac{(\pi mkT)^{1/2}}{\pi \sigma^2} \quad (\text{B2})$$

$$\chi = \frac{1 - b\rho/8}{(1 - b\rho/4)^3} \quad (\text{B3})$$

But the interactions among real molecules are not of a rigid-sphere type, making the above equations ineffective for real gases. Enskog used “thermal pressure” from the compressibility isotherms to calculate $b\rho\chi$:

$$b\rho\chi = \frac{1}{R} \left(\frac{\partial VP}{\partial T} \right)_v - 1 \quad (\text{B4})$$

Figure B1: Left: At the center of the pore, gas density is close to the bulk methane density. Towards the wall, the density increases as a result of the intermolecular forces of attraction between gas molecules and the pore wall. Decrease in the pore diameter shifts the gas density at the center away from the bulk density. Average density increases sharply for the pore radii less than 1 nm. The radial density profile shown here is calculated at $P = 5000$ psi and $T = 373$ K. **Right:** Gas viscosity at the center is close to the bulk viscosity and increases towards the pore walls, because of the dense packing of molecules. The effect is pronounced for smaller pores. The radial viscosity profile shown here is calculated at $P = 5000$ psi and $T = 373$ K.

where R is the gas constant, P , V , and T are the pressure, volume, and temperature. The Peng-Robinson equation of state in a simple cubic form is given by:

$$P = \frac{RT}{V - b'} - \frac{a(T)}{V(V + b') + b'(V - b')} \quad (\text{B5})$$

where $a(T)$ is the attractive force parameter, expressed as a function of temperature, the critical properties and the acentric factor of the gas:

$$a(T) = a(T_c)\alpha(T) \quad (\text{B6})$$

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (\text{B7})$$

$$\alpha(T) = [1 + m(1 - T_r^{0.5})]^2 \quad (\text{B8})$$

$$b' = 0.07780 \frac{RT_c}{P_c} \quad (\text{B9})$$

$$m = 0.37464 + 1.54226\omega - 0.26997\omega^2 \quad (\text{B10})$$

where T_c , P_c , and ω are the critical temperature, critical pressure, and acentric factor, respectively. Putting eq. (B5) into eq. (B4) we get:

$$b\rho\chi = \frac{V}{R} \left[\frac{R}{V - b'} + \frac{a(T_c)[m + m^2(1 - T_r^{0.5})]}{V(V + b') + b'(V - b')} \frac{1}{(TT_c)^{0.5}} \right] \quad (\text{B11})$$

Appendix C: Surface Diffusion Ratio

Assuming that slip flow and Knudsen flow are negligible, the total flux (flow rate per unit cross-sectional area) through a nanopore is the result of: (a) adsorbed gas surface diffusion because of the concentration difference along the length of the pore, and (b) gas flow due to pressure gradient in the nanopore.

Adsorbed gas surface diffusion (J_s): According to the Stephan-Maxwell model, chemical potential gradient drives surface diffusion and the corresponding flux is given by:

$$J_s = -L_m \frac{\zeta_{ms} C_s}{M} \frac{\partial \mu}{\partial l} \quad (C1)$$

where L_m is the gas mobility in mol.s/kg, ζ_{ms} is the correction factor, and μ is the chemical potential in J/mol. Assuming that the gas is ideal, the chemical potential can be expressed as:

$$\mu = \mu_0 + RT \ln p \quad (C2)$$

Combining eqs. (C1) and (C2) and neglecting the correction factor, the mass flux contribution from the surface diffusion is given by:

$$J_s = -D_s^0 \frac{C_s}{Mp} \frac{\partial p}{\partial l} \quad (C3)$$

where $D_s^0 = L_m RT$ and D_s^0 is the surface diffusion coefficient when the gas coverage is zero and is given by:

$$D_s^0 = 8.29 \times 10^{-7} T^{0.5} \exp \left(-\frac{\Delta H^{0.8}}{RT} \right) \quad (C4)$$

Gas flow due to pressure difference (J_p): Mass flux for an ideal gas in a circular tube is derived from the Hagen-Poiseuille law as:

$$J_p = \frac{\rho r^2}{8\mu} \frac{\partial p}{\partial l} \quad (C5)$$

where the density ρ is given by $\rho = PM/RT$
So, surface diffusion ratio is given by:

$$\text{Surface diffusion ratio} = \frac{J_s}{J_s + J_p} \quad (C6)$$

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