Supplementary Information

Nanomodel visualization of fluid injections in tight formations

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Section 1: Fabrication and characterization of the nanomodel

Figure S1. Nanomodel fabrication procedures. (a) Schematic of the nanomodel design. (b) (c) nanoporous media fabrication, where nanopores (75 nm wide and 50 nm deep) are fabricated through E-beam lithography and RIE ethching. (d) DRIE etching of the reservoir (200 μ m wide and deep) and thermocouple microchannels (400 μ m wide and deep). (e) Inlet/outlet holes drilled for reservoir microchannels. (f) Anodic bonding of the chip after using Piranha solution (H₂SO₄:H₂O₂ = 3:1) cleaning the photoresist.

The nanomodel was fabricated on silicon wafer (chip design is shown in Figure S1a). To fabricate the nanoporous media on the wafer, E-beam lithography (Vistec EBPG 5000+ Electron Beam Lithography System) was firstly used to generate the nanoporous pattern on the ZEP-520A resist. After that, the pattern was etched by RIE (Oxford PlasmaPro 100 Cobra ICP-RIE) to be 50 nm deep, as shown in Figure S1b and c. On each chip, there were 10 identical nanoporous media distributed along the microchannel reservoirs. After the nanoporous media was fabricated, the chip was cleaned in a Piranha solution (H_2SO_4 : H_2O_2 = 3:1) for 20 min. AZ9260 photoresist was then spin-coated on the wafer to fabricate deep microchannels and thermocouple channels. We used deep reactive ion etching (DRIE, Oxford Instruments PlasmaPro Estrelas100 DRIE System) to etch the channels to the targeting depths (Figure S1d). Afterwards, inlet and outlet holes were drilled on the silicon substrate of the microchannels, as shown in Figure S1e. The silicon wafer and a piece of 2.2 mm thick borosilicate glass were then cleaned in the Piranha solution (H_2SO_4 : H_2O_2 = 3:1) for another 20 min, and bonded together through anodic bonding (AML AWB-04 Aligner Wafer Bonder) to seal channels, as shown in Figure S1g. Bonding chips was at 673.15 K and vacuum with a voltage of 600 V for 10 min (total charge reaching ~1000 mC). Lastly, the chip was cut into the designed shape with a dicing machine (Disco DAD3220 Automatic Dicing Saw).



Figure S2. Nanomodel pore feature characterization. *w* represents pore width and L_B represents block width on the 2-D nanomodel. In our model, *w* = 75 nm and L_B = 1000 nm.

Two parameters were quantified for the nanomodel: porosity (φ) and permeability (K). The porosity was calculated through:

$$\varphi = \frac{Total \ pore \ area}{Total \ porous \ media \ area} = \frac{w^2 + 2wL_B}{\left(w + L_B\right)^2} = 13.47\%$$
(1)

The permeability was calculated through:

$$K = \frac{\varphi r^2}{8\tau} \tag{2}$$

Where r is the hydraulic radius of the nanopore, and was calculated through the pore width w (75 nm) and pore depth h (50 nm):

$$r = \frac{hw}{h+w} = 30 \ nm \tag{3}$$

au is the tortuosity. With this geometry, the value was quantified to be 1.5, and permeability was thus calculated to be 10.2 μ D through eq. (2).



Section 2: Experimental setup and procedures

Figure S3. Diagram of the experimental setup for N₂ and CO₂ flooding tests. The nanofluidic chip was mounted on a manifold to connect microchannels with pipes. Pressures of gas as well as oil were closely controlled through ISCO syringe pump, and monitored through pressure transducers. Temperature on the chip was introduced through a copper heater controlled by a water bath (323.15 K), and monitored by thermocouples inserted into the chip close to the nanoporous media.



Figure S4. Diagram of the experimental setup for CO₂ huff-and-puff tests.

To perform the flooding tests, the system (Figure S3) was firstly vacuumed at 2 x 10^{-7} MPa (PFPE RV8) for 3 hrs at room temperature (293.15 K) to ensure oil filling fully into the nanoporous media (i.e., no air trapping in the nanoporous media). After that, the oil was injected into one microchannel through syringe pump (TELEDYNE ISCO MODEL 260D, resolution at 0.001 MPa), as well as the nanoporous media at 1 MPa. Due to the capillary force, the filling would stop at the entrance of the nanoporous media on the gas channel side. Then gas at targeting pressure was injected into another microchannel. During the gas injection, oil was kept at the same pressure with gas to avoid any unexpected flooding below the targeting gas pressure. To start the flooding test, oil pressure was reduced to 5 MPa (taking less than 3 s). Flooding phenomena were observed directly through an optical microscope (Leica DM 2700M) and camera connected (Leica DMC 2900).

To perform the huff-and-puff tests (Figure S4), after vacuuming and oil injection, the oil microchannel was purged by air at 0.8 MPa for 1 hr to clean any residual oil, ensured by the vanishing of any fluorescence signals in the microchannel. The system was then vacuumed for another 1 hr to ensure no air trapped in the system. Afterwards, the gas was injected into both microchannels at targeting pressures, followed by sealing for 1 hr to allow sufficient gas diffusion into nanoporous media. In the end, the gas pressure was reduced to targeting value (1 MPa) to produce oil from the nanoporous media.

Section 3: Capillarity calculation and Lenormand phase diagram quantification

The capillary pressures between the gas phase and oil were calculated using the Young–Laplace equation, which has been validated at nanoscale in previous works¹⁻²:

$$P_{Ca} = \gamma \left(\frac{\cos\theta_h}{h/2} + \frac{\cos\theta_w}{w/2} \right) \tag{4}$$

Where P_{Ca} is the capillary pressure between the gas and oil phase, γ is the interfacial tension, h is the channel height, 50 nm, w is the channel width, 75 nm, θ_h and θ_w are the contact angle at channel height and width dimensions (close to zero).

Table 1 shows P_{Ca} calculated for all cases discussed in the main text:

Table 1 Capillary pressure calculation for different tests. The values of interfacial tensions are calculated from previous literatures³⁻⁴.

Gas species	Gas pressure (MPa)	Oil pressure (MPa)	Pressure drop (MPa)	Interfacial tension (mN/m)	Capillary pressure (MPa)	
N _{2 (flooding)}	5	5	0	21.7	1.45	
N _{2 (flooding)}	5.5	5	0.5	21.5	1.43	
N _{2 (flooding)}	6	5	1	21.3	1.42	
N _{2 (flooding)}	6.5	5	1.5	21.1	1.41	
N _{2 (flooding)}	7	5	2	21	1.40	
N _{2 (flooding)}	9	5	4	20.2	1.35	
N _{2 (flooding)}	11	5	6	19.5	1.30	
CO _{2 (huff-and-puff)}	5	4.05	0.95	14.2	0.95	
CO _{2 (huff-and-puff)}	7	6.29	0.71	10.7	0.71	
CO _{2 (huff-and-puff)}	1	-0.42	1.42	21.3	1.42	

To quantify the fingering effect during N₂ flooding, two parameters (mobility ratio, M and capillary number, Ca) were calculated:

$$M = \frac{K_{oil}/\mu_{oil}}{K_{gas}/\mu_{gas}}$$
(5)

$$Ca = \frac{\mu_{gas}v}{\gamma} \tag{6}$$

Where K_{gas} and K_{oil} are the permeability of gas and oil in the nanomodel (same in our case), μ_{gas} and μ_{oil} are the dynamic viscosity of gas and oil, ν is the characteristic velocity (displacing rate in our case), and γ is the interfacial tension.

Table 2 shows log M and log Ca calculated for all cases discussed for nitrogen

N ₂	Gas	Oil	Interfacial	Displacing	Μ	Ca	logM	logCa
pressure	viscosity	viscosity	tension	rate	(10 ⁻³)	(10 ⁻⁹)		
(MPa)	(µPa.s)	(µPa.s)	(mN/m)	(um/s)				
7	20.1	4200	21	5.71	4.78	5.46	-2.32	-8.26
9	20.5	4200	20.2	27.50	4.88	27.91	-2.31	-7.55
11	21	4200	19.5	71.43	5.00	76.90	-2.30	-7.11

flooding:

Table 2 Mobility and capillary number calculation for nitrogen immiscible flooding. The N₂ viscosity is from NIST webbook⁵. Displacing rate is estimated through the experimental results shown in Figure 2 in the main text. Oil viscosity is from previous literature⁶.

The results are shown in Lenormand phase diagram (Figure S5), indicating capillary fingering effects in the nanomodel for nitrogen flooding.



Figure S5. Lenormand phase diagram shows nitrogen flooding in the nanomodel brings capillary fingering effect, as observed in our experiments.

Section 4: Quantification of the miscible film displacement length and diffusion length in shale reservoirs



Figure S6. Schematic of film-wise displacement in the reservoir.

To simply calculate the speed of film-wise displacement (v), we considered a 1-D transport diagram as shown in Figure S6. v is thus can be expressed as:

$$v = \frac{dL_{gas}}{dt} = \left(P_{gas} - P_{oil}\right)\varphi r^2 / 8\tau \left[\left(\mu_{gas} - \mu_{oil}\right)L_{gas} + \mu_{oil}L_R\right]$$
(7)

Where L_{gas} is the length of gas phase traveling in the reservoir, P_{gas} is the gas injection pressure, P_{oil} is the reservoir oil pressure, φ is the porosity of the reservoir, r is the mean pore radii, τ is the reservoir tortuosity, μ_{gas} is the gas viscosity, μ_{oil} is the oil viscosity, L_R is the total reservoir length (or the reservoir length between the injection and production wells). By integrating eq. (7) with initial condition ($L_{gas} = 0$ when t = 0), and considering the condition $\mu_{oil} \gg \mu_{gas}$

(more than 100 times), one gets the expression for L_{gas} as a function of recovery time (t):

$$L_{gas} = L_{R} - \sqrt{L_{R}^{2} - \frac{\varphi r^{2} (P_{gas} - P_{oil})}{4\mu_{oil}\tau}t}$$
(8)

The diffusion length $({}^{L_{Diff}})$ follows Fick's law, and can be expressed as a function of recovery time (t):

$$L_{Diff} = 2\sqrt{\frac{D}{\tau}t}$$
(9)

Where the gas diffusivity into oil is D, as the diameter of gas molecules (e.g., CO₂, ~0.3 nm) are still much smaller than the pore size (e.g., 60 nm in our case). We assume bulk diffusivity (~ $5 \times 10^{-9} m^2/s$)⁷ can still be applied here. The tortuosity (7) will also affect the effective diffusivity in a periodic porous system⁸.

By calculating the difference (ΔL) between L_{Diff} and L_{gas} :

$$\Delta L = L_{Diff} - L_{gas} = 2\sqrt{\frac{D}{\tau}t} - L_R + \sqrt{L_R^2 - \frac{\varphi r^2 (P_{gas} - P_{oil})}{4\mu_{oil}\tau}t}$$
(10)

One can find that when:

$$0 < t < \frac{16DL_R^2}{\tau \left[4D + \frac{\varphi r^2 (P_{gas} - P_{oil})}{4\mu_{oil}\tau} \right]^2}$$
(11)

 ΔL is always greater than 0. This indicates that within the initial certain range of time, the gas diffusion length is always longer than the gas film displacement

length. For the nanomodel in this work, $L_R = 10^{-3} m$, $\varphi = 0.13$, r = 30 nm, $\tau = 1.5$ and $P_{gas} - P_{oil} = 6 MPa$, the time range is thus calculated to be 0 < t < 23 s. From the experiments, we noticed that the gas breakout happens first as fingers, while film displacement captures the fingers at ~20 s (Figure 3 (A)). The order of magnitude match here indicates that the calculation can describe the gas breakout phenomena well. For a real shale reservoir, parameters are available from orders of magnitude, where L_R is on the order of 10 m, φ is on the order of 0.1, r is on the order of 100 nm, τ is on the order of 1 and $P_{gas} - P_{oil}$ is on the order of 10 MPa. The range is thus calculated to be $0 < t < 10^7 s$ (~4 months). Therefore, within the first few months for the miscible flooding in a low pressure reservoir, gas breakout could happen first, while the miscible flooding will follow the initial production.

It is noting that, the analytic model here separates the pressure driven fluid viscous transport and the free molecular diffusion effect for a simplification of calculation and comparison. These two effects are inherently coupled and can be potentially solved with computational fluidic methods. The model also simplifies the flow boundary conditions, to strictly follow the non-slip boundary condition from classical fluid mechanics for both gas and liquid phases, as the pore scale here is at 60 nm, and the pore surface is smooth (roughness at ~0.2 nm). At a smaller sub-10 nm pore scale, the fluid slip boundary condition might be important to be considered, especially for the gas phase. The slip boundary condition will in general lead to a reduced viscous transport resistance in nanopores. However, these simplifications are not expected to affect the order of magnitude estimations, as well as the qualitative conclusions demonstrated here.

Section 5: N₂ flooding at 12 MPa



Figure S7. High pressure nitrogen flooding (12 MPa nitrogen and 10 MPa oil) result. The FOR is ~31 %.

Section 6: CO₂ diffusion in the nanomodel during the huff-and-puff injection



Figure S8. Schematic of the initial CO_2 diffusion during the production (puff) stage. (a) the initial and boundary conditions for CO_2 concentration calculations. (b) CO_2 concentration distribution for an initial injection pressure of 7 MPa in the nanoporous media at different time. (c) CO_2 concentration distribution for an initial injection pressure of 5 MPa in the nanoporous media at different time.

The diffusion of CO₂ from the nanoporous media to the microchannel would happen during the production stage. This problem can be quantitatively solved through 1-D diffusion equation. Given the diffusivity of CO₂ in oil $(5 \times 10^{-9} m^2/s)$ and tortuosity (1.5), the effective diffusivity in the nanomodel is $3.33 \times 10^{-9} m^2/s$. When CO₂ was dissolved in the nanoporous media at a CO₂ gas pressure of 7 MPa, the liquid oil pressure was 6.3 MPa due to capillarity (quantified in section 3). The initial CO₂ solubility was found to be 103 kg/m³ (C^{I}) from the previous literature⁷. At the targeting production pressure (1 MPa), the oil pressure was at -0.4 MPa, and the final CO₂ solubility (C^{E}) was 0. As the pressure drawdown was continuously from 7 MPa to 1 MPa in the microchannel, to simplify the calculation, we assumed that the solubility at the boundary of the nanomodel was

$$\frac{dC}{dC} = \frac{-(C^I - C^E)}{-(C^I - C^E)}$$

linearly changing (i.e., dt t , where t is total time for the pressure depletion). Based on these conditions, the CO₂ concentration distributions at different time are shown in Figure S7(b). At 20 s, the average CO₂ concentration (

$$C^{A} = \frac{\int_{0}^{L} C(x) dx}{I}$$

L) in the nanoporous media was ~63 kg/m³. While at 200 s, the average CO₂ concentration was only ~13 kg/m³. Similarly, for an initial gas injection pressure at 5 MPa, the oil pressure was at 4 MPa due to capillarity (section 3), the CO₂ solubility is 25 kg/m³. At 20 s, the CO₂ concentration distribution is shown in Figure S8, where the average value was ~15 kg/m³.

Oil displacement in the nanomodel initiated from 7 MPa (Fig. 4A), while at 5 MPa, during depressurization there was no oil displacement. The reason is the significant change of CO₂ solubility at different injection pressures because of capillarity in nanoconfinement. Here, when injected CO₂ was at 5 MPa, the oil pressure was actually 4 MPa due to capillarity (section 3). Under this condition, the CO₂ concentration in the oil is expected to be 25 kg/m³ as determined elsewhere⁷. Similarly, with CO₂ at 7 MPa, the oil pressure was 6.3 MPa (section 3), and CO₂ concentration reaches 103 kg/m³. After a 20 s production, the CO₂ pressure was reduced to 1 MPa. The oil was under tension at -0.4 MPa (capillary pressure ~1.4 MPa, section 3), and CO₂ solubility in oil approaches zero. This leads to (i) CO₂ accumulating and generating bubbles within the nanoporous media, pushing oil out, and/or (ii) CO₂ diffusing out from the nanoporous media. The former requires supersaturated CO₂ accumulating and overcoming capillary pressure to form gas bubbles (1 MPa), with a minimum CO₂ density at 17 kg/m³. A 5 MPa CO₂ injection

pressure leads to low average remaining CO_2 concentration in oil after a 20 s production (~15 kg/m³). Bubbles was thus not likely to form. While for the initial CO_2 injection pressure at 7 MPa, the average remaining CO_2 concentration is at 63 kg/m³ greater than 17 kg/m³ (section 6). Bubbles were observed to grow during the production stage to displace oil (Fig. 4A). The total production time would also affect the oil recovery. For example, at the same 7 MPa CO_2 injection pressure but for a 200 s production (compared to 20 s), no trapped oil was observed to be produced from the nanomodel. The reason is due to the gas diffusion eliminating most CO_2 in the nanoporous media (average remaining CO_2 concentration is only 13 kg/m³). Likewise, bubbles were unable to generate and displace oil.

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