Fracture-Matrix Interaction, Fluid Flow and Chemical Movement in Shale*

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Search and Discovery Article #51564 (2019)**
Posted May 6, 2019

*Adapted from oral presentation given at 2019 AAPG Southwest Section Annual Convention, Dallas, Texas, April 6-9, 2019
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Abstract

Even after hydraulic fracturing, the issues of steep initial decline and low overall recovery of hydrocarbons (oil and gas) from fine-grained reservoirs affect the economic sustainability of shale resource development. In low-permeability unsaturated fractured shale, fluid flows predominantly through the interconnected fracture network, with some fluid imbibing into the neighboring shale matrix. Imbibition (driven by capillary pressure gradient) advectively transports chemicals from fracture into matrix. Diffusion (driven by concentration gradient) can diffusively transport chemicals into/from the matrix. Once in the matrix, sorbing chemicals can sorb onto matrix rock. All these interacting processes (imbibition, sorption, and diffusion) control fluid flow and chemical transport in fractured shale. Microscopic characteristics of porous matrix – pore shape, pore-size distribution, pore connectivity – influence macroscopic behavior of fluid flow and chemical transport and can therefore affect the fate of injected fracturing fluids, flowback and produced fluids, as well as the exploration of hydrocarbons in hydraulically-fractured shales. Using an innovative and complementary laboratory approaches, such as imbibition and diffusion tests employing nano-sized tracer recipe followed with microscale mapping of tracers, our work indicates the limited fracture–matrix interactions in fractured shale, with low pore connectivity of nm-sized shale matrix pores and the consequent limited (sub-mm near the fracture face) accessible porosity and anomalous diffusion to the stimulated fracture network and producing wellbore.

References Cited


Zhang et al., 2019, Small Angle Neutron Scattering, in press.

Fracture-matrix Interaction, Fluid Flow and Chemical Movement in Shale

C3PM
Center for Collaborative Characterization of Porous Media

(Max) Qinhong Hu
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• Production decline and fracture-matrix interaction

• Scientific issues across scales
  ✓ Connectivity
  ✓ Wettability
  ✓ Accessibility
  ✓ Diffusivity
  ✓ Tortuosity
  ✓ Permeability
  ✓ Capillarity
  ✓ Fracability
  ✓ Productivity

• Summary
Ongoing Shale Revolution

Loucks et al. (2009)
Shale Revolution: Facts

- Steep initial decline (both gas and oil: $\frac{2}{3}$ after 1 yr)
- Low recovery (shale gas: <30%; tight oil: <10%)
- 40% wells (~90,000) drilled in US uneconomic
- 25% wells produce ~80% output ("80-20 Rule")
Hypothesis: Fracture-matrix Interactions Control Production Behavior in Stimulated Shale

- Fracture-matrix interactions control production behavior.

- Microscopic mechanisms control macroscopic production.

- 10+ orders of magnitude in scale.

- nm-μm pore networks.

- Matrix feeding of hydrocarbons from Bulk to Surface Zones.

- Fracture-matrix interaction.
Earlier Fracture-Matrix (F-M) Interaction Studies

Field observation (preferential flow in a fracture network) of dye distribution in unsaturated fractured tuff at Yucca Mt.

My work on fracture-matrix interaction starts with this rock.

$t_m = 4 \mu \alpha \phi \frac{d_m^2}{k}$
Pore Structure: Geometry and Topology

Percolation theory: the mathematics of how macroscopic properties emerge from local (microscopic) connections

- **Surface Zone:** ~70%
- **Bulk Zone:** ~0.1%

**Effective porosity/Total porosity** ($\phi_e/\phi$)

- **Isolated Porosity**
- **Connected Porosity**
- **Edge Porosity**
- **Infinite Cluster**
- **Backbone**
- **Dead Ends**
Unique Dual-Connectivity Zones of Shale: Multiple Evidence

Wood’s metal impregnation (600 MPa)

1 cm cube

Size GRI (500-841 μm)

MICP

Exp. slope = -0.489
Theo. slope = -0.466

~1/1,000

Diffusion

Imbibition

Barnett shale: 7,136 ft (2,175 m)
saturated diffusion time: 24 hr

Experiment

Theoretical

Re exterior data
Re interior line 1
Re interior line 2
Re background (avg +/- std dev)
Fitted Dc: 1.46E-11 m²/s
Fitted Dc: 1.46E-13 m²/s

Bulk Zone
Surface Zone

1 cm cube

Size B (177-500 μm)
Size C (75-177 μm)
Hu et al., JCH, 2012; JGR, 2015

Surface (~400 µm; ~70%) Mudrock

~2000 µm (~70%) Sandstone

Distance from sample edge (fracture face)

REV

χ

φ

φ_e

χ : correlation length

β and ν: percolation exponents — 0.41 and 0.88 for 3-D

• Larger proportion of closed pores for larger sample sizes

• Assess pore connectivity by measuring effective porosity of different sample sizes

Edge-accessible Effective Porosity

φ(h) = φ_e \begin{cases} (h / χ)^{β/ν} & h < χ \\ 1 & h > χ \end{cases}
Multiple Approaches to Studying Pore Structure (Geometry and Topology)

- Pycnometry of gas and hydrophilic / hydrophobic fluids (DI water; API brine; n-decane; isopropyl alcohol IPA or tetrahydrofuran THF) for fluid-accessible effective porosity of a range of sample sizes ($\mu$m – 10 cm) (UTA)

- Fluid (DI water; API brine; n-decane; IPA or THF) and tracer imbibition with respect to sample bedding direction and initial moisture content (UTA)

- Edge-accessible porosity after tracer vacuum-saturation and high-pressure intrusion (UTA)

- Liquid and gas diffusion, under ambient and high-pressure / high-temperature conditions (UTA)

- Mercury Injection Capillary Pressure analysis and hysteresis (UTA; CUG)

- Low-pressure gas adsorption isotherm and hysteresis (Univ. of Tokyo, Japan; CDUT, CAS-GIG and CUG, China; UT Austin; Kansas State Univ.)

- Water vapor adsorption isotherm and hysteresis (UTA)

- Nuclear Magnetic Resonance Cryoporometry (Lab-Tools, Ltd., UK; Niumag Co., China; UPC)

- Ar ion milling Field Emission-SEM (FE-SEM) and QEMSCAN (Quantitative Evaluation of Materials by Scanning) mapping, correlated with tracer mapping to study Dalmatian wettability and connectivity of shale composition pore systems (Hitachi; CUP-Beijing, CAS-GIG, and CGS-O&G, China)

- 2-D imaging/mapping after Wood's metal impregnation (Univ. Hannover, Germany; EPMA, Switzerland)

- Microtomography (high-resolution, synchrotron, nano-CT) (PNNL-EMSL; Swiss Light Source; Univ. Hannover; Saitama Univ., Japan; CUP-Beijing, RIPED, China)

- Focused Ion Beam/SEM (FIB-SEM) imaging (PNNL-EMSL; CUP-Beijing; CGS-O&G)

- Small-Angle Neutron Scattering (U)SANS (NIST; ORNL; LANL; Mianyang) and Small-Angle X-Ray Scattering (Shanghai SSRF; Beijing BSRF, Jilin Univ., China)

- Pore-scale network modeling (Iowa State Univ.; Wright State Univ.; Kansas State Univ.)

- Physics-based production decline analyses (DrillingInfo; IHS-Fekete Harmony; Eclipse, Kappa)
Pore Structure, Wettability, and Hydrocarbon Movement

Accessory data
- TOC
- Maturity
- Mineralogy
- Pyrolysis
- Well logging
- Production
- Contact angle
- Imbibition
- QEMSCAN for Dalmatian pattern

✓ Gas and liquid pycnometry
✓ MICP (different sizes)
✓ Gas sorption isotherm
✓ (U)SANS
✓ NMRc
✓ GRI matrix k
✓ FE-SEM
✓ FIB-SEM
✓ Wood’s metal
✓ Vacuum saturation for edge-accessible porosity
✓ Imbibition
✓ Wettability tracers
✓ Imbibition
✓ Diffusion
✓ Core & m-block flooding

Pore structure
Wettability
Hydrocarbon movement
Total worldwide rig counts: ~4000

Peak rig counts (June 2014): 1861

Weekly rig counts (4/5/2019) +19 to 1025
Sweet Spots and Sampling

Utica / Point Pleasant

different maturity
Vacuum Saturation: Sample Size and Fluids

- Measure porosity & densities for large and irregular samples
- Use different (polar and non-polar) fluids: DI water, n-decane, toluene, isopropyl alcohol IPA or THF

Boiled & cooled DI water
Effective porosity ↓ sample size

>99.992% vacuum for 2 d

4” full-size core
First cut as many as **15** 1-cm sized cubes

Then crush ALL fragments into different size fractions

- Epoxyed for imbibition, diffusion
- Back-up (vac sat with tracers; traced imbibition & diffusion)
- Vac sat (DI water)
- Vac sat (n-decane : toluene)
- Vac sat (THF)
- MICP

**A Range of Sample Sizes for Different Tests**

- FE-SEM; SANS
- 220-grit sandpaper for contact angle
- & Ro
### A Range of Sample Sizes

<table>
<thead>
<tr>
<th>Size designation</th>
<th>Sieve mesh</th>
<th>Size fraction (diameter)</th>
<th>Equivalent spherical dia. (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder/Plug</td>
<td></td>
<td>2.54 cm dia.; any height (e.g., 3 cm)</td>
<td>(24394)</td>
</tr>
<tr>
<td>Cube</td>
<td></td>
<td>1.0 cm</td>
<td>9086</td>
</tr>
<tr>
<td>Size X</td>
<td>8 mm to #8</td>
<td>2.38 - 8 mm</td>
<td>5190</td>
</tr>
<tr>
<td>GRI+</td>
<td>#8 to #12</td>
<td>1.70 - 2.38 mm</td>
<td>2040</td>
</tr>
<tr>
<td>Size A</td>
<td>#12 to #20</td>
<td>841 - 1700 μm</td>
<td>1271</td>
</tr>
<tr>
<td>GRI</td>
<td>#20 to #35</td>
<td>500 - 841 μm</td>
<td>671</td>
</tr>
<tr>
<td>Size B</td>
<td>#35 to #80</td>
<td>177 - 500 μm</td>
<td>339</td>
</tr>
<tr>
<td>Size C</td>
<td>#80 to #200</td>
<td>75 - 177 μm</td>
<td>126</td>
</tr>
<tr>
<td>Powder</td>
<td>&lt;#200</td>
<td>&lt; 75 μm</td>
<td>&lt; 75</td>
</tr>
<tr>
<td>Size D</td>
<td>#200 to #625</td>
<td>20 - 75 μm</td>
<td>47.5</td>
</tr>
<tr>
<td>Size E</td>
<td>&lt;635</td>
<td>&lt;20 μm</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>

**Overlaps Surface Zone and Bulk Zone for mudrocks**

- 1-in plug
- 10-mm cube
- 1.70-2.36 mm
- 0.84-1.7 mm
- 500-841 μm
- 177-500 μm
- 75-177 μm

Porosity: 0.80±0.42% (N=31)
Permeability: 1.11±0.57 µD (N=35)

MICP
Porosity: 0.59%
Permeability: 1.08 µD

K for Grimsel Granodiorite Benchmark

David et al., GJI, 2018a, b

Gases vs. liquids
Steady-state vs. transient
Confining pressure

30 labs from 8 countries
1 hr – 5 d
Shengli Oilfield, Sinopec Liye#1 3782.63 m

Hu et al., Petro. Explor. Develop., 2017

Multiple nm-μm Pore Systems

GRI: #20 - #35 mesh

MICP: cube

Laminated calcareous mudrock

Porosity: 7.96%

OM Pores
\( L_t = 9.19 \text{ nm} \), \( k = 3.22 \times 10^{-20} \text{ m}^2 \)

InterP (carbonates, pyrite)
\( L_t = 24.7 \text{ nm} \), \( k = 6.32 \times 10^{-20} \text{ m}^2 \)

Microfractures/lamina
\( L_t = 9.49 \mu \text{m} \), \( k = 2.39 \times 10^{-15} \text{ m}^2 \)

Microfractures/laminas
\( L_t = 27.4 \mu \text{m} \), \( k = 5.74 \times 10^{-15} \text{ m}^2 \)

IntraP (dissolution)
\( L_t = 2.08 \mu \text{m} \), \( k = 2.72 \times 10^{-16} \text{ m}^2 \)

InterP, dissolution
\( L_t = 411 \text{ nm} \), \( k = 1.32 \times 10^{-17} \text{ m}^2 \)
Fracture Apertures: μm-CT vs. MICP

Shengli Oilfield
laminated calcareous mudrock

China University of Petroleum

μm CT
16.18 μm  6.35 μm

MICP
0.71 - 27.4 μm
Berea sandstone
Median pore-throat size: 23.8 µm
Connectivity: good

Barnett (Blakely #1 7136', limestone)
Median pore-throat size: 22.4 nm
Connectivity: poor

Wood’s Metal Intrusion, Imaging, and Mapping

~0.4% of pore spaces is connected

Bulk Zone
Surface Zone

Stefan Dultz
Josef Hoffmann
Wood’s Metal Intrusion, Imaging, and Mapping

Barnett shale (Blakely #1 7,219’) with cracks

Hu et al., JCH, 2012; JGR, 2015

6,000 bars (2.35 nm)

Bulk Zone

Surface Zone

50 µm

1 µm

10 µm
Mixed Wettability and Associated Pore Structure

- **Dalmatian** wettability behavior
- **Variable at um scale**
- **Complex interplay of wettability and pore size**

Fluid spreading behavior in a typical shale

Contact angle: 43°  
Spreading: modest

Contact angle: <3°  
Spreading: excellent

- **OM particles (22%)**
- **OM-hosted pores (8.6%)**
- **Inorganic minerals**
- **Water-filled pores (0.2%)**

Wolfcamp: SEM (Wall et al., 2016)
Wettability-based Fluids and Tracers

- **API brine (8 wt% NaCl+2 wt% CaCl$_2$) [water-wet]**
  - ReO$_4^-$ (0.553 nm)
  - Anionic Sb-complex (0.89 nm)
  - Cationic Ru-complex (1.0 nm)
  - CdS nanoparticles (5–10 nm)

- **n-decane: toluene [oil-wet]**
  - Organic-I
  - Organic-Re
  - CeF$_3$ nanoparticles (10–12 nm)

- **Tetrahydrofuran–zewittering**
  - Ru-complex (2.42 nm)

Hu et al., J. Nano. Nanotech., 2017
Different Tracer Tests for Process-Level Understanding

- Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)
- Imbibition
- Vacuum saturation
- Diffusion
- High-pressure impregnation

Hu et al, Vadose Zone J., 2002
Laser Ablation-ICP-MS Tracer Mapping

10 mm-sided cube

Bottom (tracer-contacted) face conc. check

Conc. check of top face (either Parallel or Transverse to lamination)

Interior face (2D mapping)

3D mapping

Cut the sample dry to expose the interior face

Remove epoxy on the wall to map side face

Tracer mapping grids

Hu et al., JGR, 2015
Non-wetting Fluid: Effective Porosity Effect

Re background: $1.29 \pm 1.24$ mg/kg

Cs background: $8.85 \pm 4.20$ mg/kg

Ce background: $51.0 \pm 33.6$ mg/kg

Barnett 7109
Brine
Imbibition
94 hrs
Wetting Fluid: Molecular Size Effect

**Eagle Ford shale**

n-decane

Vac sat + High-pressure intrusion

Oil-wet pores: 2.8-20 nm pore throat dia.

**H₂O**: 0.32 nm  
**CH₄**: 0.38 nm  
**Aromatics**: 1-3 nm  
**Asphaltene**: 5-10 nm

(Nelson, 2009)

**Hu et al., Geofluids, 2018**

**CH₃(CH₂)₆CH₂I**  
1.393 nm × 0.287 nm × 0.178 nm

**1.273 nm × 0.919 nm × 0.785 nm**

**I bkgd**: 2.54 ± 2.67 mg/Kg  
**Re bkgd**: 1.55 ± 1.46 mg/Kg
Small Angle Neutron Scattering (SANS)

- Detect both connected and closed pores
- Obtain full-scale nm-μm pore diameters
- Quantify hydrophilic vs. hydrophobic pore space
- Investigate reservoir P-T condition

Yang et al., 2017; Sun et al., 2017; Zhao et al, SR, 2017; Zhang et al., 2019
<table>
<thead>
<tr>
<th>Formation</th>
<th>TOC</th>
<th>MICP (1cm cube)</th>
<th>(U)SANS (grains: 177-500 μm)</th>
<th>MICP (grains: 177-500 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Bakken</td>
<td>Bakken</td>
<td>13.7wt.%</td>
<td>2.29%</td>
<td>11.69%</td>
</tr>
<tr>
<td>Sample #4</td>
<td></td>
<td></td>
<td>(1.1 nm – 20 μm)</td>
<td>(3.4nm - 50 μm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.20%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.10%</td>
</tr>
</tbody>
</table>

(U)SANS: Fluid-Wettable Pore Space

<table>
<thead>
<tr>
<th>Formation</th>
<th>TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utica (Late Ordovician) (R₀&lt;0.5%)</td>
<td>Utica (R₀=0.82%)</td>
</tr>
<tr>
<td>Middle Bakken (late Devonian)</td>
<td></td>
</tr>
</tbody>
</table>

Zhang et al., 2019 (under prep.)
Production Decline in Log-Log Space

Fractures: -1
Matrix: -1/2 or -1/4
Fracture-Matrix interaction: -2/3
Summary and Application

- **Dual connectivity at ~500 µm** from sample edge (rapid initial decline & low recovery; completions for complex fracture network; refrac; shut-in)
- **Mixed wettability** at µm scale; oil than water (modification for enhanced recovery)
- **Dual flow paths** in 3-D space: >10-50 nm hydrophilic pore network at slow rate; ~5 nm hydrophobic pore network with rapid rate but size exclusion (production of small-sized hydrocarbons)