Impact of Carbonate Mineral Dissolution on Hydrocarbon Transport in Shales

Youssef Elkady and Anthony R. Kovscek

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Outline

- Introduce the problem
- What has been done: Literature Review
- Areas to Tackle
- Necessary tools: Theory and Lab Practices
- Preliminary Work
- Conclusions and Future Course of Action
CO2 Potential on Carbonates-Rich Shales?

- Gas potential: Marcellus, Barnett, and Haynesville alone ~ 2500 TCF (DOE/NETL 2009)
  - 20-30% recovery
- Oil potential: 4.9 MMBbl/d in 2015 about 52% US oil production (EIA, 2017)
  - 5-10% recovery

- Reason:

(Wu and Sharma, 2015)
CO2 Potential on Carbonates-Rich Shales?

- Gas potential: Marcellus, Barnett, and Haynesville alone ~ 2500 TCF (DOE/NETL 2009)
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- Reason:
  (Wu and Sharma, 2015)

- Room for improvement:
  - pH of water in scCO2: 2.80 – 2.95
  (Toews et al., 1995)

(Kohli, Unpublished)
Current Literature (1/2)

Waterfall Diagram

Shale Revolution →

Acid Utilization in Calcareous Shale

Current Production Strategy

Multi-stage Hydraulic Fracturing

Horizontal Drilling

Producing at Shale Matrix Permeability

Recovery

Alternative Stimulation Inhibition

Stanford University
Current Literature (1/2)

Waterfall Diagram

- Shale Revolution
- Acid Utilization in Calcareous Shale
- Current Production Strategy
  - Multi-stage Hydraulic Fracturing
  - Horizontal Drilling
- Recovery
  - Producing at Shale Matrix Permeability
- Rapid and Complete Dissolution
- Detachment of non-soluble mineral
- Bimodal to Tri-modal Pore Distribution
- 30-70% Fracture Surface Hardness Reduction

Wu and Sharma (2015): 24% wt. carbonate samples and 3% wt. HCl in 3% wt. KCl
Recovery

Multi-stage Hydraulic Fracturing
Horizontal Drilling
Producing at Shale Matrix Permeability

Shale Revolution

Acid Utilization in Calcareous Shale ??

Current Production Strategy

1000 md-ft Conductivity at Low Closure

Stresses (1000psi)

Sample Initial Hardness Influence

Severe Reduction in Conductivity (10 to 100 md-ft) at High Closure Stresses (4000psi)

Cash et al. (2016)
Current Literature (2/2)

Waterfall Diagram

Shale Revolution

Acid Utilization in Calcareous Shale ??

1000 md-ft Conductivity at Low Closure

Non-Uniform Etching along Calcite Streaks

Current Production Strategy

Sample Initial Hardness Influence

Tripathi and Pournik (2014)

Recovery

Multi-stage Hydraulic Fracturing

Horizontal Drilling

Cash et al. (2016)

Producing at Shale Matrix Permeability

Severe Reduction in Conductivity (10 to 100 md-ft) at High Closure Stresses (4000 psi)

Low Conductivity Post-Acidizing

Stanford University

Alternative Stimulation Inhibition

1000 md-ft

1000 psi
Recovery

Multi-stage Hydraulic Fracturing

Horizontal Drilling

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Shale Revolution

Current Production Strategy

Acid Utilization in Calcareous Shale ??

1000 md-ft Conductivity at Low Closure Stresses (1000psi)

Non-Uniform Etching along Calcite Streaks

Increased Fracture Complexity

Tripathi and Pournik (2014)

Gomaa et al. (2014), and Grieser et al. (2007)

Low Conductivity Post-Acidizing

Severe Reduction in Conductivity (10 to 100 md-ft) at High Closure Stresses (4000psi)

Reduce Breakdown Pressure

Cash et al. (2016)

Stanford University

Acid Utilization

Sample Initial Hardness Influence

Low Conductivity

Non-Uniform Etching along Calcite Streaks

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Low Conductivity Post-Acidizing

Severe Reduction in Conductivity (10 to 100 md-ft) at High Closure Stresses (4000psi)

Reduce Breakdown Pressure

Cash et al. (2016)
Summarizing Injecting Acid?

- Increased in pore volume and surface area
- Non-uniform etching
- Increased Fracture Complexity
- Reduction in breakdown pressure

- Reduction in Fracture Surface Toughness
- Ineffectiveness at high closure stresses
- Rock Strength Damage or Softening

Increased in pore volume and surface area
Non-uniform etching
Increased Fracture Complexity
Reduction in breakdown pressure
Reduction in Fracture Surface Toughness
Ineffectiveness at high closure stresses
Rock Strength Damage or Softening
Theory (1/4)

CT Imaging

\[
\frac{l}{l_0} = \exp^{-\mu h}
\]

\[CT = 1000 \frac{\mu - \mu_w}{\mu_w}\]

\[\phi = \frac{CT_{kr} - CT_{ar}}{CT_k - CT_a}\]
CT Imaging

\[ \frac{l}{l_0} = \exp^{-\mu h} \]

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Pulse Decay

\[ P_1 - P_f = \Delta P \left[ \frac{V_2}{V_1} + V_2 \right] e^{-at} \]

Adsorption Influence

\[ \phi_a = \frac{\rho_s}{V_{std}} \frac{1 - \phi}{c_g \rho} \frac{q_L p_L}{(p_L + p)^2} \]

\[ k = \frac{s_1 \mu L c_g}{f_1 A \left( \frac{1}{V_u} + \frac{1}{V_d} \right)} \]

Klinkenberg Correction

\[ k_a = k_{inf} \left( 1 + \frac{K_p}{P} \right) \]
Theory (3/4)

CT Imaging
\[ \frac{I}{I_0} = \exp^{-\mu h} \]
\[ CT = 1000 \frac{\mu - \mu_w}{\mu_w} \]
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Pulse Decay
\[ P_1 - P_f = \Delta P \left[\frac{V_2}{V_1} + V_2\right] e^{-\alpha t} \]

Adsorption Influence
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Klinkenberg Correction
\[ k = \frac{s_1 \mu L c_g}{f_1 A \left(\frac{1}{V_u} + \frac{1}{V_d}\right)} \]

Rock Mechanics
\[ E = \frac{F/A}{\Delta l/l_0} \]

Weak rock have weak cohesion
\[ C_o = 2S_o \left[(\mu_i^2 + 1)^{1/2} + \mu_i\right] \]
Theory (4/4)

CT Imaging

\[ \frac{l}{l_0} = \exp^{-\mu h} \]

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Rock Mechanics

\[ E = \frac{F/A}{\Delta l/l_0} \]

Well Testing (Simulation)

E300 Black Oil Compositional 2D Model

Gridding Scheme

Weak rock have weak cohesion

\[ C_o = 2S_0 \left[ (\mu_i^2 + 1)^{1/2} + \mu_i \right] \]

\[ s = \frac{k_e k_{r \phi h}}{141.2qB\mu} \Delta P_s \]
Preliminary Work

- Built core holder and designed experimental setup for pulse decay, krypton/CO2 injection, and CT scanning

- Conducted shale porosity and permeability measurements (characterization stage) and their evolution with increasing net effective stress

- Investigated potential high storage capacity zones using 3D Computed Tomography (CT) imaging and Quantitative X-Ray Diffraction (QXRD) mineralogical analysis
Experimental Workflow - Sample Preparation (1/3)

Vacuum Oven ~ 1-2 weeks
PTFE sleeve and aluminum foil
Sample Preparation
Experimental Workflow - Sample Preparation (1/3)

Sample Preparation

Vacuum under CT scanner
Experimental Workflow – Pulse Decay (2/3)

Pulse Decay Setup - Permeability
Experimental Workflow – Pulse Decay (2/3)

Pulse Decay Setup - Porosity
Experimental Workflow – Storage & CT Imaging (3/3)

- Inject Krypton for porosity/storage capacity
- Wait for pressure equilibrium

\[ \varnothing = \frac{CT_{Kr} - CT_{ar}}{CT_{Kr} - CT_a} \]

(Aljamaan, 2017)
Experimental Results: Pulse Decay Permeability

Pressure pulse 2 (300 psi effective stress & 457 psi pore pressure)

- Downstream Pressure
- Upstream Pressure
- Temperature (°C)
Experimental Results: Pulse Decay Permeability

5x increase in effective stress resulted in ~1.5 order of magnitude reduction in permeability

<table>
<thead>
<tr>
<th>Effective Stress (Psi)</th>
<th>Liquid-like vertical permeability (nD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1000</td>
</tr>
<tr>
<td>600</td>
<td>700</td>
</tr>
<tr>
<td>1200</td>
<td>N/A</td>
</tr>
<tr>
<td>1500</td>
<td>20</td>
</tr>
</tbody>
</table>
Experimental Results: Pulse Decay Porosity

<table>
<thead>
<tr>
<th>Effective Stress (Psi)</th>
<th>Porosity (%)</th>
<th>Avg. Equilibrium Time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.3*</td>
<td>N/A</td>
</tr>
<tr>
<td>600</td>
<td>3.5</td>
<td>12</td>
</tr>
<tr>
<td>1200</td>
<td>2.8</td>
<td>11</td>
</tr>
<tr>
<td>1500</td>
<td>1.7</td>
<td>21</td>
</tr>
</tbody>
</table>

*zero effective stress porosity calculated from mineral composition and grain density of averaged QXRD mineralogy data from 1ft interval above and below zone from which our sample was cored

Increasing effective stress to 1500 Psi results in a ~2.5 multiple reduction in porosity
### Experimental Results: QXRD and 3D CT Image

<table>
<thead>
<tr>
<th>Mineralogy</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>1-2</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0-1</td>
</tr>
<tr>
<td>Ankerite or Excess Calcium Dolomite</td>
<td>4-5</td>
</tr>
<tr>
<td>Calcite</td>
<td>50-60</td>
</tr>
<tr>
<td>Clay</td>
<td>20</td>
</tr>
<tr>
<td>Quartz</td>
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**Experimental Results: QXRD and 3D CT Image**

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<table>
<thead>
<tr>
<th>Mineralogy</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>red</td>
</tr>
<tr>
<td>Ankerite or Excess Calcium Dolomite</td>
<td>green</td>
</tr>
<tr>
<td>Calcite</td>
<td>light blue</td>
</tr>
<tr>
<td>Clay and Quartz</td>
<td>dark blue</td>
</tr>
</tbody>
</table>
Experimental Results: 2-D Storage Capacity Zones

2-D Slice
Experimental Results: 2-D Storage Capacity Zones
Experimental Results: 3-D Storage Capacity Construction

- Exponential Color Scale
  - Displays 3 different porosity scales
    - 10-30% near Ankerite-rich zones
    - 1-10% in most of sample
    - <1% possibly in high Quartz regions
- Krypton storage capacity = 3.9%
  - Within experimental error from helium’s at 300psi effective stress
  - Adsorption could account for additional capacity observed
Conclusion

- Workflow established for characterizing permeability, porosity, and mineralogy

- Pulse Decay:
  - Severe matrix permeability reduction (1000nD to 20nD) at high effective stress
  - 2.5 multiple reduction in porosity (4.3% to 1.7%) at high effective stress
  - Independent QXRD derived porosity in agreement with pulse decay trend

- QXRD and CT Imaging:
  - Location of different carbonates and high density minerals within W2 sample

- Krypton Storage Capacity Study:
  - Associates high storage zones with high carbonate zones
  - Storage capacity of 3.9%, similar to helium porosimetry results from pulse decay experiment
Future Work

- Use triaxial setup to measure Young’s modulus and fracture sample

- Saturate fractured core with crude oil

- Inject supercritical CO2 then introduce water (create acid) to assess enhanced recovery using mass balance and CT imaging techniques

Courtesy of Guenther Glatz
Acknowledgements

- Tony
- Elliot and Shale group: Hamza, Beibei, and Bolivia
- Arjun Kohli and Guenther Glatz
- SUPRI-A members
- SUPRI-A affiliates for financial support
Thank You!

Question?
Appendix
Simulation Work & Problem Framing
Simulation Work (Grid)
Simulation Work (Grid)
Simulation Work (Fluid and Rock Properties)

Ge and Ghassemi et al., (2012) estimated stimulation going up to 200 times the original matrix permeability in Barnett samples. Assumed x100 and logarithmic decrease in permeability away from fracture until matrix permeability.
Simulation Work (Results)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
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<tbody>
<tr>
<td>$q$</td>
<td>0.1</td>
<td>MSCF/D</td>
</tr>
<tr>
<td>$B$</td>
<td>0.66</td>
<td>$ft^3$/SCF</td>
</tr>
<tr>
<td>$\mu$</td>
<td>0.029</td>
<td>cp</td>
</tr>
<tr>
<td>$h$</td>
<td>100</td>
<td>ft</td>
</tr>
<tr>
<td>$K_r$</td>
<td>0.5</td>
<td>--</td>
</tr>
<tr>
<td>$k$</td>
<td>11.2</td>
<td>$nD$</td>
</tr>
<tr>
<td>$\Delta P_s$</td>
<td>case dependent</td>
<td>psi</td>
</tr>
</tbody>
</table>

$$ s = \frac{k_e k_r h}{141.2 q B \mu} \Delta P_s $$

Skin Values using common log gridding

<table>
<thead>
<tr>
<th>Fracture Aperture (mm)</th>
<th>Stimulated Distance Away from Fracture (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>-4.11</td>
</tr>
<tr>
<td>1.5</td>
<td>-4.12</td>
</tr>
<tr>
<td>2.5</td>
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Simulation Work – Grid Sensitivity Study (Results)

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</table>

The different gridding schemes show no influence on skin results up to 1m away from the fracture surface on each end and for all reasonable fracture apertures.
Framing the Problem

Decisions

- Acid as Fracing Fluid?
- Acid Concentration?
- Acid after Fracing?
- Acid with Proppant?
Framing… (2/3)

Decisions

Acid as Fracing Fluid?
Acid Concentration?
Acid after Fracing?
Acid with Proppant?

Research Uncertainties

Fracture Surface Softening
Insoluble Mineral Detach
Wettability Alteration
Rock Strength
Closure Stress Influence
Gas Desorption / Diffusivity Rate

Practical Uncertainties

Cost of Reactive Fluid
Transportation
Well Integrity
Compatibility with Proppant
Framing… (3/3)

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- Fracture Surface Softening
- Insoluble Mineral Detach
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- Compatibility with Proppant
Framing… (3/3)

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- Cost of Reactive Fluid
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Value Measures in Lab

- Conductivity/Permeability (md-ft/md)
- Recovery (ml)
- Skin

Cost of Reactive Fluid

Compatibility with Proppant
Framing… (3/3)

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- Cost of Reactive Fluid
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Value Measures in Lab
- Conductivity/Permeability (md-ft/md)
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- Skin

Ultimate Value
- Field Recovery (bbl)
- Ultimate Value
From an Experimentalist Standpoint...

Research Uncertainties

- Fracture Surface Softening
- Insoluble Mineral Detach
- Wettability Alteration

Value Measures in Lab

- Conductivity/Permeability (md-ft/md)
- Recovery (ml)
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What do we know?