Pore Network Modeling of Carbonate Acidization

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Introduction

- Over 60% world’s hydrocarbon reserves found in carbonates
- Acid injection dissolves rock near the wellbore, ideally forming conductive wormholes
- With proper design, 88% of stimulations improve production (Crowe et al., 1992)
Acidizing Strategy

Compact dissolution (too slow)

Uniform dissolution (too fast)

Fredd and Fogler, 1998

Wormholes (intermediate)

Optimum $Da_{mt} = 0.29$ (Fredd and Fogler, 1999)

$$Da_{mt} = 6.33 \left( \frac{LD}{Q} \right)^{(2/3)}$$
Previous Pore Network Models

Fredd and Fogler, 1998

**Experimental**

- 0.06 cc/min, $D_{am} = 0.70$
- 0.3 cc/min, $D_{am} = 0.23$
- 1 cc/min, $D_{am} = 0.11$
- 0.01 cc/min, $D_{am} = 2.31$

**Simulations**

- 0.2 cc/min, $D_{am} = 0.07$
- 1 cc/min, $D_{am} = 0.02$
- 0.09 cc/min, $D_{am} = 0.11$
- 0.01 cc/min, $D_{am} = 0.49$
Our Pore Network Approach

Extract pore networks from real carbonate cores

Simulate many networks together using mortar coupling

Direct comparison with core experiments
Network Extraction

2.3 mm

1 mm

1 mm
1. Enforce Mass Balance for Pressure

\[ Q_i = \sum_j q_{ij} = \sum_j \frac{g_{ij}}{\mu} (P_i - P_j) = 0 \]

\[ Q = \pi r^4 \frac{1}{8L} \frac{1}{\mu} \Delta P \]
2. Solve Advection-Diffusion Equation

Flow In

\[ C_{\text{in}} \]

Flow Out

\[ C_{\text{pore}} \]

\[ V_{p_i} \frac{dc_i}{dt} = \sum_i D_{e} a_{ij} \frac{\Delta c_i}{L_{ij}} + \sum_i c_i q_{ij} \]

Accumulation = diffusion + advection
3. Pore Scale Reaction

$CaCO_3(s) + 2H^+ \rightarrow Ca^{++} + CO_2(aq) + H_2O$

- Reaction is almost infinitely fast
- Limited by the rate of acid transport
- “Mass transfer limited” regime

Barnes, 2012
Mass Transfer Coefficients in COMSOL

\[ C_{\text{wall}} = 0 \]

Stokes equation for flow field

Advection-diffusion equation for concentration (steady state)

\[ n = Q(C_{\text{in}} - C_{\text{out}}) \]

\[ n = K_{\text{mt}} A (C_{\text{bulk}} - C_{\text{wall}}) \]

\[ K_{\text{mt}} = Q(C_{\text{in}} - C_{\text{out}})/AC \]

1 micron

Carbonate Rock

Stokes equation for flow field

Advection-diffusion equation for concentration (steady state)

\[ n = Q(C_{\text{in}} - C_{\text{out}}) \]

\[ n = K_{\text{mt}} A (C_{\text{bulk}} - C_{\text{wall}}) \]

\[ K_{\text{mt}} = Q(C_{\text{in}} - C_{\text{out}})/AC \]

1 micron
Mass Transfer Correlation

\[ Sh = \text{convective mass transfer/diffusive mass transfer} = K_{mt} \frac{L}{D} \]

\[ Pe = \text{advective transport/diffusive transport} = \frac{L}{D} \]

\[ Sh = K \log (C Pe + 1) \]
4. Increase Pore Size and Conductivity

\[ V_{\text{Dissolved}} = \frac{K_{\text{mt}}}{2} A \Delta C \Delta t \Delta p = \sqrt{SA_{\text{new}} / SA_{\text{old}}} \quad r_{\text{old}} \]

\[ g = \pi r^4 / 8 \]
5. Merge Pores

- Growing pores will eventually overlap
- Network approach creates error
- Merge pores
Merging Method

\[ V_{\text{in1}} = V_{\text{in2}} + V_{\text{in3}} \]

\[ \text{Error} = |Q_{\text{true}} - Q_{\text{merged}}| / Q_{\text{true}} \]
Summary of Simulation

- Step 1: Solve pressure
- Step 2: Acid transport (advection/diffusion)
- Step 3: Acid consumption using pore-scale mass transfer coefficient
- Step 4: Enlarge pore space
- Step 5: Merge pores according to pore merging criterion

Repeat from step 1 until breakthrough
Wormholing
(Intermediate Injection)

- Videos removed
Uniform Dissolution (Fast Injection)  

Face Dissolution (Slow Injection)  

Concentration, mol/L
Results: Sphere Packs

- 0.2 mm$^3$/sec, $D_{am} = 0.26$
- 1.0 mm$^3$/sec, $D_{am} = 0.09$
- 0.005 mm$^3$/sec, $D_{am} = 3.05$
1000 Grain Sphere Pack Simulations Experiments (Fredd and Fogler, 1999)

General Experimental
Optimum $Da_{mt} = 0.29$

Simulation Optimum $Da_{mt} = 0.26$

$$1/Da = 1/\left[6.33 \left(\frac{LD_c}{Q}\right)^{2/3}\right]$$
Application To Carbonate Rock Types

- **Pink Desert**: 1.15 mm
- **Indiana LS**: 2.23 mm
- **Edwards White**: 2.24 mm

**Diagram Descriptions**:
- Domain split into 1/8ths (simulation time)
- Entire Domain Simulated
- Domain split into 1/8ths (connectivity)
Results: Pink Desert Carbonate (cont.)

![Graph showing permeability ratio vs. pore volumes injected]

- **0.1 mm$^3$/sec**: $D_{mt} = 0.48$
- **1.0 mm$^3$/sec**: $D_{mt} = 0.1$
- **0.005 mm$^3$/sec**: $D_{mt} = 3.51$

**Face Dissolution**

**Wormholing**

**Uniform Dissolution**

- $Q = 0.005$ mm$^3$/sec
- $Q = 0.1$ mm$^3$/sec
- $Q = 1$ mm$^3$/sec
Results: Pink Desert Carbonate

Simulation Optimum $Da/m_t = 0.48$

Experimental Optimum $D = 0.42$

$1/Da_{mt} = 1/\left[6.33\left(\frac{LD_c}{Q}\right)^{(2/3)}\right]$
Indiana Limestone

Pore Volumes To Breakthrough, $K_x/K_0 = 10$

Simulation Optimum $Da_{\text{opt}} = 0.76$

Experimental Optimum $Da_{\text{opt}} = 0.22$
Pore Volumes to Breakthrough ($K_x/K_0 = 30$)

Simulation Optimum $Da_{\text{mt}}$
$= 0.25$

Experimental Optimum $D$
$\alpha_{\text{mt}} = 0.22$
Conclusions

• Developed novel pore network model of carbonate acidization
  – Pore merging algorithm
  – Mass-transfer coefficient

• Prediction of optimal $D_{am}$ in sphere packs and several SLB carbonate samples

• Discovered non-Newtonian flow field unlikely cause of improved SXE performance

• Dynamic relationship between viscosity and diffusion provides best explanation
Backup Slides
Future Work (cont.)

Integration of PNM findings with Two-Scale continuum model

\[ \frac{K}{K_{\downarrow} \beta^{12}} = k_{\downarrow} cte \left( \frac{\varepsilon_{\downarrow} \beta}{1 - \varepsilon_{\downarrow} \beta} \right)^{13} \]

\[ \frac{K}{K_{\downarrow} 0} = (\varepsilon/\varepsilon_{\downarrow} 0)^{\gamma} \left( \varepsilon(1-\varepsilon_{\downarrow} 0)/\varepsilon_{\downarrow} 0 \right)^{\gamma_2 \beta} \]

Static relationship between \( k \) and \( \varphi \) derived from bundle of capillary tubes or empirically in the uniform dissolution regime.

Pore network models can generate a dynamic relationship \textit{a priori} for different Damkohler numbers.
Future Work (cont.)

Mortar coupling to go to much larger domain sizes

Mehmani et al., 2012

Domain the size of core for 1:1 comparison with core flood experiments

Coupling with near-wellbore model to predict acidizing response in full reservoir simulators
Results on Other Networks
Carbonate Rock Types

- Edwards Yellow: Pending simulation
- Winterset LS: Unconnected, even as 1/8th subsections
- Austin Chalk: Poorly connected. No Acidizing Experiments
At large enough domain size, it obviously becomes connected again. However the whole CT scan is not connected according to our PNM extraction software. Only one of the 8 cubic subsections is connected.
Indiana Limestone Tracers

\[ \frac{C_{\text{end}}}{C_0} \] vs.

Pore Volumes Injected

- Newtonian Simulation
- Experiment
Indiana Limestone RTD

Residence Time Distribution Chart

- Indiana Limestone Experiment
- Indiana Simulation

Dimensionless Time, \( T/T_{@C_{\text{outlet}=0.5}} \)

\( E(T_0) \):
- 2.50E+00
- 2.00E+00
- 1.50E+00
- 1.00E+00
- 5.00E-01
- 0.00E+00

Values range from 0.00E+00 to 4.50E+00 on the x-axis.
Edwards White Tracers

![Graph showing the relationship between pore volumes injected and Concentration ratio (C_end/C_0) for Edwards White Tracers. The graph includes two curves: one for the Network and another for Experimental data.](image)
Pink Desert Tracers

![Graph showing the relationship between Pore Volumes Injected and $C_{end}/C_0$. The graph includes data points for Newtonian and Power Law Experiments.]

- Newtonian Experiments
- Power Law Experiments

Change legend to DI Water (check) vs. polymer
PD Entire Thing dominant flow path
Polymers: Early Breakthrough + Tailing

- Tracers conducted in Zakaria et al. (2015) are polymer (displacing water)

- Tracers conducted with polymers frequently break through more quickly
  - Inaccessible Volume Effect: Large polymer molecules cannot travel inside smaller pores (Sorbie et al., 1973)
  - Average velocity of polymer is higher because size of polymers keeps them out of the slowest flow regions (Dirk et al., 1980)
Power Law Flow Field
Back of the Envelope: Bundle of Capillary Tubes + Power Law Flow Field

- 2 capillary tubes

Newtonian Case; assume:

\[ Q_{\text{total}} = 17 \text{ m}^3/\text{sec} \]

Then:

\[ Q_1 = 16 \text{ m}^3/\text{sec} \]
\[ Q_2 = 1 \text{ m}^3/\text{sec} \]
### Back of the Envelope: Bundle of Capillary Tubes + Power Law Flow Field

<table>
<thead>
<tr>
<th>Newtonian Case</th>
<th>Non-Newtonian Case ( (n=0.641) )</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_{\text{total}} = 17 \text{ m}^3/\text{sec} )</td>
<td>( Q_{\text{total}} = 17 \text{ m}^3/\text{sec} )</td>
<td>( \Delta Q_{\text{total}} = 0 )</td>
</tr>
<tr>
<td>( Q_1 = 16 \text{ m}^3/\text{sec} )</td>
<td>( Q_1 = 16.3 \text{ m}^3/\text{sec} )</td>
<td>( \Delta Q_1 = 0.3 = +1.87% )</td>
</tr>
<tr>
<td>( Q_2 = 1 \text{ m}^3/\text{sec} )</td>
<td>( Q_2 = 0.69 \text{ m}^3/\text{sec} )</td>
<td>( \Delta Q_2 = -0.31 = -31% )</td>
</tr>
</tbody>
</table>

\[
\frac{Q_{\text{big}}}{Q_{\text{total}}} = \frac{3\frac{1}{n}}{R_{\text{big}}^{3\frac{1}{n}} + R_{\text{small}}^{3\frac{1}{n}}}
\]

Conclusion: Power law fluids do not change the flow field in large throats or dominant flow paths; they do, however, significantly slow flow in small pores.
More Modeling Details
Pore-Scale Mass Transfer Coefficients

\[
Sh = \left[ \left( 1 - \frac{L_{\text{throat}}}{2L_{\text{pore}}} \right) \left( 0.0048 (Pe) + 23.95 \right) \right] + \left[ \left( \frac{L_{\text{throat}}}{2L_{\text{pore}}} \right) (6.603 \ln (Pe) + 7.691) \right]
\]
Viscoelastic Modeling
CFD Modeling of Single-Phase Flow

- Sinusoidal geometry extremely useful
  - Constructing pore throat for network
  - Simple porous medium

- FEM used to solve momentum equations
  - Input Constitutive model (e.g. Upper Convected Maxwell)
  - Obtain pore throat equations for flow

Momentum:
\[
\rho \left[ \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right] = -\nabla P + \nabla \cdot \mathbf{T}
\]

Upper Convected Maxwell Model:
\[
\tau \left[ \frac{\partial \mathbf{T}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{T} - \nabla \mathbf{u} \cdot \mathbf{T} - \mathbf{T} \cdot \nabla \mathbf{u}' \right] + \mathbf{T} = \eta \left( \nabla \mathbf{u} + \nabla \mathbf{u}' \right)
\]

- Deborah number

\[ De = \frac{Q \tau}{\pi R \Delta t} \quad \text{def elastic/viscous} \]

Arfshapoer 2013
CFD Results: Pore-level equations

- CFD results of different aspect ratio ($\alpha$), and dimensionless throat length ($\Lambda = \frac{2\pi h}{\lambda}$)

Arfsharpoor 2013
Network Modeling Results

Experiment-a

- Beadpack, 100-110 micron, φ=0.39, K=4.2 D
- Pusher 700, 1000 ppm, 1% NaCl

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>0.75</td>
</tr>
<tr>
<td>α</td>
<td>2.0</td>
</tr>
<tr>
<td>λ (s)</td>
<td>0.057</td>
</tr>
<tr>
<td>n₂</td>
<td>2.54</td>
</tr>
<tr>
<td>μ_p° (cp)</td>
<td>8</td>
</tr>
<tr>
<td>μ_∞ (cp)</td>
<td>1.02</td>
</tr>
<tr>
<td>μ_max (cp)</td>
<td>40</td>
</tr>
<tr>
<td>τ_y (s)</td>
<td>0.086</td>
</tr>
</tbody>
</table>

1000 ppm, 0.1% NaCl

1000 ppm, 1% NaCl

500 ppm, 1% NaCl

Arfshapoor 2013
Two-Scale Continuum Integration
Two Scale Continuum Models

\[
\frac{K}{\beta_1} = k cte \left( \frac{\varepsilon_1}{1 - \varepsilon_1} \right)^{\gamma_3}
\]

\[
\frac{K}{K_0} = \left( \frac{\varepsilon}{\varepsilon_0} \right)^{\gamma} \left( \frac{\varepsilon(1 - \varepsilon_0)}{\varepsilon_0} \right)^{\gamma_2 \beta}
\]

**Static** relationship between \( k \) and \( \phi \) derived from bundle of capillary tubes or empirically in the uniform dissolution regime.

Pore network models can generate a **dynamic** relationship \textit{a priori} for different Damköhler numbers.

Golfier et al., 2002

Maheshwari, 2013