Evaluating the Potential for Petroleum Hydrocarbons to Induce Gas Ebullition in Sediments

10th International Conference on the Remediation and Management of Contaminated Sediments

Session D.5 Ebullition, Abstract 214

10:30-10:55 AM, February 13, 2019

New Orleans, LA

Karl Rockne¹,² PhD, PE, BCEE

Morvarid Khazraee Zamanpour¹

¹Department of Civil and Materials Engineering
University of Illinois at Chicago

²Chemical, Bioengineering, Environmental and Transport Processes
National Science Foundation
Overview

1. Gas Ebullition 101
2. Biogenic Gas Fracture Mechanics Model of Gas Ebullition
3. Biotransformations of Petroleum Hydrocarbons
4. Evaluation of Potential for PHs to drive ebullition
5. Conclusions
Gas Ebullition

WHAT IS IT?

• Gas ebullition results from methane gas production by mixtures of *Bacteria* and *Archaea* at rates sufficient to cause bubble nucleation, growth, fracture, and rise in sediment

• A complex relationship governed by biology, chemistry, and physics

WHY IS IT IMPORTANT?

• Microorganisms produce CH$_4$ from the decomposition of organic matter

• CH$_4$ bubble growth -> elastic fracture releasing bubbles that rise to the surface

• Ebullition can entrain HOCs and heavy metals, releasing them to the surface
II) Biogenic Gas Fracture Mechanics Model of Gas Ebullition
Gas Ebullition: Biology

- Gas formation $f(\text{Temp, microbial structure})$
  - Hydrogenotrophic Archaea: dominant at high Temps
    - $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
  - Acetoclastic Archaea: dominant at lower Temps
    - $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_4 + \text{CO}_2$
BGFM Model of Bubble expansion in cohesive sediment:

Mass transport is governed by the **Diffusion-Reaction equation**:

\[
\frac{\partial C}{\partial t} = D_{\text{eff}} \nabla^2 C + S
\]

- \( C \): methane solute concentration
- \( S \): methane source strength in sediment
- \( D_{\text{eff}} \): the effective methane diffusion coefficient in sediment

\[
\log(S) = 23 - 1.6 \log(\rho_s) - 3,800 \left( \frac{1}{T} \right) - 2,500 \left( \frac{S_{\text{labite}}}{T} \right) + 2,600 \left( \frac{S_{\text{labite}}^2}{T} \right) + 1.5 \log(S_{\text{labite}}) + 0.28 \log(\gamma_0 + \gamma_1 T + S_{\text{labite}})
\]

- \( \rho_s \): Wet bulk density (kg m\(^{-3}\))
- \( T \): Average temperature during the measurement period (K)
- \( S_{\text{labite}} \): COD/OC
- \( \gamma_0 = 0.8083 \) and \( \gamma_1 = -0.0026 \)

Methane gas inside the bubble is assumed to behave as an ideal gas \((P_g = C_b R T)\), and its **mass conservation equation** over the bubble surface \((s)\) within the sediment-bubble transport system is:

\[
V_b \frac{\partial C_b}{\partial t} + C_b \frac{\partial V_b}{\partial t} = \oint \mathbf{n} D_{\text{eff}} \nabla C \, ds
\]

- \( V_b \): bubble volume
- \( C_b \): gas concentration inside the bubble

Bubble volume can be determined by deformation of the surrounding sediment by bubble growth according to the **elasticity equation**:

\[
\rho_s \frac{\partial^2 \mathbf{u}}{\partial t^2} - \nabla \cdot (\nabla C \mathbf{u}) = F_g = 0
\]

- \( \mathbf{u} \): displacement vector
- \( \rho_s \): sediment bulk density
- \( F_g \): the gravity force, which is assumed to be negligible.
Biogenic Gas-Fracture Mechanics (BGFM) Ebullition Model

**FEM model in COMSOL-MATLAB:** Two-phase elastic expansion-fracture growth coupled with CH₄ production & transport

**Boundary/Initial Conditions**

- Far field methane ($C_\infty$) is constant controlled by environment
- Methane on the **bubble surface in equilibrium** with bulk gas phase inside the bubble using Henry’s law: $C_b = k_H C$
- Methane concentration surrounding the bubble is equal to the far field concentration at $t = t_0$

<table>
<thead>
<tr>
<th>Site characteristics</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water depth</td>
<td>3 (m)</td>
</tr>
<tr>
<td>Sediment depth above bubble</td>
<td>0.10 (m)</td>
</tr>
<tr>
<td>Effective diffusion coefficient ($D_{eff}$)</td>
<td>$1 \times 10^{-9}$ (m²/s)</td>
</tr>
<tr>
<td>Temperature range ($T$)</td>
<td>278(K) $&lt; T &lt; 303(K)$</td>
</tr>
<tr>
<td>Bulk density ($\rho_s$)</td>
<td>1400 (kg/m³)</td>
</tr>
<tr>
<td>Young’s modulus ($E$)</td>
<td>$1.4 \times 10^8$ (Pa)</td>
</tr>
<tr>
<td>Poisson ratio ($\nu$)</td>
<td>0.3</td>
</tr>
<tr>
<td>Fracture stiffness factor ($K_{IC}$)</td>
<td>$300$ (Pa/m¹/₂)</td>
</tr>
<tr>
<td>Far field methane concentration ($C_\infty$)</td>
<td>3.4 (mol/m³)</td>
</tr>
</tbody>
</table>

* From Gardiner et al. 2003
Bubble Growth: LEFM predicts an oblate spheroid
Concentration distribution in sediment during bubble growth
Impact of Sediment Properties on Bubble Size at Fracture

\[ P_c = \frac{K_{ic}^{6/5} \pi^{3/5} (1 - v^2)}{12^{1/5} (E V_b)^{1/5}}. \]
Impact of sediment mechanical properties on bubble growth: Fracture stiffness ($K_{IC}$)
Global Sensitivity Analysis:
Sediment strength > Methanogenic biokinetics

Input range:
- Methane production: $7 \times 10^{-7} - 6.12 \times 10^{-6}$ mol/m³/s
- Young’s modulus: 28 - 252 kPa
- Poisson ratio: 0.12 to 0.48
- Fracture toughness: 60 to 540 Pa.m¹/²
- Yield stress: 200 to 8000 Pa
III) Biotransformations of Petroleum Hydrocarbons
Anaerobic degradation of Petroleum Hydrocarbons

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Δ(G^0) (w) kJ/reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 Complete oxidation</td>
<td>(4C_{16}H_{34} + 128H_2O \rightarrow 64CO_2 + 196H_2)</td>
</tr>
<tr>
<td>R2 Oxidation to Acetate + H(_2)</td>
<td>(4C_{16}H_{34} + 64H_2O \rightarrow 32CH_3COO^- + 32H^+ + 68H_2)</td>
</tr>
<tr>
<td>R3 Oxidation to Acetate</td>
<td>(4C_{16}H_{34} + 30H_2O + 34CO_2 \rightarrow 49CH_3COO^- + 49H^+)</td>
</tr>
<tr>
<td>M1 Syntrophy</td>
<td>(CH_3COO^- + H^+ + 2H_2O \rightarrow 2CO_2 + 4H_2)</td>
</tr>
<tr>
<td>M2 Acetoclasty</td>
<td>(CH_3COO^- + H^+ \rightarrow CO_2 + CH_4)</td>
</tr>
<tr>
<td>M3 Hydrogenotrophy</td>
<td>(4H_2 + CO_2 \rightarrow CH_4 + 2H_2O)</td>
</tr>
<tr>
<td>Overall</td>
<td>(4C_{16}H_{34} + 30H_2O \rightarrow 15CO_2 + 49CH_4)</td>
</tr>
</tbody>
</table>
Ring reduction to potential methanogenic substrates

One-megadalton metalloenzyme complex in *Geobacter metallireducens* involved in benzene ring reduction beyond the biological redox window

Simona G. Huwiler, Claudia Löfler, Sebastian E. L. Anselmann, Hans-Joachim Stärk, Martin von Bergen, Jennifer Fleischler, Reinhard Rachal, and Matthias Boll

Department of Microbiology, Faculty of Biology, University of Freiburg, 79104 Freiburg, Germany; Department of Analytical Chemistry, Helmholtz-Centre for Environmental Research – UFZ, 04318 Leipzig, Germany; Department of Molecular Systems Biology, Helmholtz-Centre for Environmental Research – UFZ, 04318 Leipzig, Germany; Institute of Biochemistry, Faculty of Life Sciences, University of Leipzig, 04103 Leipzig, Germany; and **Centre for Electron Microscopy/Anatomy, Faculty of Biology & Preclinical Medicine, University of Regensburg, 93040 Regensburg, Germany**
IV) Evaluation of Potential for PHs to drive ebullition
To have gas ebullition, you need to have **bubble growth**

What combination of **methane generation rate** and sediment **geophysical strength** is sufficient to just allow bubble growth?

![Diagram showing bubble growth and gas production rate over time.](image)
Biogenic gas production rates in PAH-contaminated sediments
As a function of Temperature; Two high rate sites/Two low rate sites
Compilation of published CH₄ generation rate data

<table>
<thead>
<tr>
<th>Source</th>
<th>Substrate</th>
<th>Mechanism</th>
<th>Starting substrate concentration (mM)</th>
<th>CH₄ produced (nmol/l)</th>
<th>Ecalibration time (s)</th>
<th>Temperature (°C)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil</td>
<td>C₂-C₅ alkanes</td>
<td>Methanogenic fermentation</td>
<td>400</td>
<td>50</td>
<td>475</td>
<td>9×10⁻⁶</td>
<td>20-25</td>
</tr>
<tr>
<td>Mature fine tuning and added in alkane</td>
<td>C₆-C₁₀ alkanes</td>
<td>Aerobic and hydroxyprotopholic methanogonism</td>
<td>0.2-0.3%</td>
<td>19-202</td>
<td>203</td>
<td>5×10⁻¹</td>
<td>32</td>
</tr>
<tr>
<td>Methanogenic naphtha</td>
<td>Toluene, xylene</td>
<td>Aerobic and hydroxyprotopholic methanogonism</td>
<td>0.96</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>35</td>
</tr>
<tr>
<td>Oil shale</td>
<td>41</td>
<td>31 from BTEX</td>
<td>232</td>
<td>310</td>
<td>1×10⁻⁴</td>
<td>32</td>
<td>40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Petroleum Hydrocarbon</th>
<th>% of articles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short chain alkanes</td>
<td>24%</td>
</tr>
<tr>
<td>Long chain alkanes (&gt;10 C)</td>
<td>31%</td>
</tr>
<tr>
<td>Mono-aromatics</td>
<td>17%</td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons (PAHs)</td>
<td>14%</td>
</tr>
<tr>
<td>Chlorinated aromatics</td>
<td>5%</td>
</tr>
<tr>
<td>Chlorinated aliphatics</td>
<td>2%</td>
</tr>
<tr>
<td>NSOs</td>
<td>7%</td>
</tr>
</tbody>
</table>

Petroleum Hydrocarbon % of articles

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Methane Generation Rate (x10⁻⁷ mmol/l/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;C₁₀</td>
<td>▲</td>
</tr>
<tr>
<td>&gt;C₁₀</td>
<td>□</td>
</tr>
<tr>
<td>BTEX</td>
<td>△</td>
</tr>
<tr>
<td>Iso-alkanes</td>
<td>△</td>
</tr>
<tr>
<td>Naphtha</td>
<td>▲</td>
</tr>
<tr>
<td>PAH</td>
<td>▽</td>
</tr>
</tbody>
</table>

10th International Conference on Contaminated Sediments
Minimal gas generation rate needed for bubble growth as a function of fracture stiffness ($K_{IC}$) and elasticity ($E$)
V) Conclusions
Conclusions:

Several **limitations** on the potential for PHs to drive gas ebullition

- **Thermodynamic** limitations on anaerobic PH biodegradability
  - Degrading aromatics and alkanes difficult **without** $O_2$
  - Competition with other more labile organic matter substrates

- **Biokinetic** limitations on methane generation
  - Limited **methanogenic substrate range**
  - Methane biokinetics strong function of Temperature

- **Geophysical** constraints on gas ebullition
  - $E$
  - $K_{IC}$
Conclusions (continued):

Given these limitations in the specific case of PHs

- **Polycyclic Aromatics**
  - Not likely even in soft mud at depths below 25 cm due to slow methane formation rates

- **Mono-Aromatics**
  - Not likely at depths below 25-80 cm due to slow methane formation rates

- **Alkanes >10 C’s**
  - Not likely at depths below 25-80 cm due to slow methane formation rates

- **Alkanes <10 C’s**
  - Methane formation rates may be sufficient for depths up to ~80 cm
Five Interconnected Grand Challenges

1. Sustainably supply food, water, and energy
2. Curb climate change and adapt to its impacts
3. Design a future without pollution and waste
4. Create efficient, healthy, resilient cities
5. Foster informed decisions and actions

65. Biokinetic and sediment structural controls on gas release from NAPL-contaminated sediments

Morvarid Khazraee Zamanpour and Karl J. Rockne
Group 2 Poster Session D.5 Wednesday 5:45-7:00