DISPOSAL OF PRODUCED WATER INTO DEPLETED OIL RESERVOIRS: ECONOMIC USE AND RISK OF USDW POLLUTION

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LOCATION AND DEPTHS OF HYDRAULIC FRACTURING ACROSS THE UNITED STATES

- The average fracturing depth across the US is 2500 m
- Many wells (6900; 16%) were fractured less than 1600 m
- 2600 wells (6%) were fractures above 900 m

CHEMICAL COMPOSITION OF PRODUCED WATER (PW)

- Ba is the most common and abundant heavy metal found in PW from hydraulically fractured shale gas reservoirs

- TDS include heavy metals and NORMs
- Organic matter includes organic fracturing additives (e.g., guar gum)

MICROBIOLOGICAL COMPOSITION OF PRODUCED WATER FROM SHALE GAS RESERVOIRS

- Biocide treatments are not effective in suppressing microbial activity
- The relative abundance of aerobic microbial species decreases in produced water with an increase in anaerobic microbial species

RISK OF USDW CONTAMINATION BY HEAVY METALS PRESENT IN PRODUCED WATER?

- Depths below surface, for completion intervals of saltwater disposal wells (2010 – 2013)
- Possible pathways for heavy metals transport from deep saline aquifers to USDW

EXPERIMENTS TO DETERMINE THE MOBILITY OF HEAVY METALS (BARIUM) IN DISPOSAL SITES

- Batch sorption experiments
- Core-flooding experiments
SORPTION OF BARIUM ON DOLOMITE AND SANDSTONE

- Ba sorption decreases with increasing salinity and temperature
- Ba sorption is higher on dolomite than on sandstone

### Tested PW compositions

<table>
<thead>
<tr>
<th>NaCl (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Mg (mg/L)</th>
<th>Guar gum (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>90,000</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1,000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>90,000</td>
<td>1,000</td>
<td>1,000</td>
<td>0</td>
</tr>
<tr>
<td>90,000</td>
<td>0</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>90,000</td>
<td>0</td>
<td>0</td>
<td>50</td>
</tr>
</tbody>
</table>

Equilibrium Ba sorptions

PREPARATION OF NATURAL AND SYNTHETIC CORE PLUGS

Preparation of synthetic plugs of uniform flow properties

<table>
<thead>
<tr>
<th>Core plug type</th>
<th>Diameter (cm)</th>
<th>Length (cm)</th>
<th>Porosity (%)</th>
<th>Permeability (mD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural dolomite</td>
<td>2.54</td>
<td>4</td>
<td>5</td>
<td>0.06 - 0.4</td>
</tr>
<tr>
<td>Synthetic dolomite</td>
<td>2.54</td>
<td>7.4</td>
<td>26.1</td>
<td>12.2</td>
</tr>
<tr>
<td>Synthetic sandstone</td>
<td>2.54</td>
<td>8.8</td>
<td>32.5</td>
<td>108.7</td>
</tr>
</tbody>
</table>

Flow properties of core plugs used for core-flooding experiments

MOBILITY OF BARIUM THROUGH DOLOMITE AND SANDSTONE ROCKS

- Ba mobility increases with increasing NaCl, Ca, and Mg concentrations
- Ba mobility is higher in dolomite aquifers than in sandstone aquifers
- Compared to the effect of salinity, guar gum has a negligible effect on the mobility of Ba

STIMULATION OF METHANGENIC CRUDE OIL BIODEGRADATION?

- Sulfate reducing bacteria (SRB)
- Nitrate reducing bacteria
- Fermentative microbes
- Hydrogen forming microbes
- Consortia of methanogenic microbes
- Acetoclastic methanogens
- Hydrogenotrophic methanogens

\[
\begin{align*}
\text{CO}_2 + \text{H}_2 &= \Delta \text{CH}_4 + \Delta \text{H}_2\text{O} \\
\text{CH}_4 + \text{H}_2\text{O} &= \Delta \text{CO}_2 + \Delta \text{H}_2
\end{align*}
\]

STUDY CASE: STILLWATER AND CUSHING OIL FIELDS OF OKLAHOMA

- Both crude oils resemble waxy crude oil containing high concentrations of heavy n-alkanes (C_{18+})

PRODUCED WATER AND CRUDE OIL COMPOSITION

<table>
<thead>
<tr>
<th>Element</th>
<th>Stillwater (mg/L)</th>
<th>Cushing (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>78.054</td>
<td>110.899</td>
</tr>
<tr>
<td>NO_3-N</td>
<td>0.3</td>
<td>0.001</td>
</tr>
<tr>
<td>Ca</td>
<td>33.300</td>
<td>53.011</td>
</tr>
<tr>
<td>Mg</td>
<td>6.913</td>
<td>11.408</td>
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<tr>
<td>SO_4-2</td>
<td>1.000</td>
<td>1.440</td>
</tr>
<tr>
<td>NO_3-N</td>
<td>0.018</td>
<td>0.018</td>
</tr>
<tr>
<td>K</td>
<td>282.76</td>
<td>83.37</td>
</tr>
<tr>
<td>Na</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>Ca</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>Mg</td>
<td>4.56</td>
<td>3.16</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Chemical composition of PWs

Produced water

Gas chromatography analysis

Three-phase separator

Produced water + nutrient solution

CO_2

Depleted oil reservoir

Stillwater and Cushing oil fields in Oklahoma

Produced water from depleted oil reservoir

Stillwater and Cushing WCs analyzed

Stills water oil field crude oil

Cushing oil field crude oil
ANAEROBIC MICRO COSM EXPERIMENTS

(a) Anaerobic chamber
(b) Microcosms kept in the incubator at 50 °C
(c) Gas chromatography analysis: headspace and remaining crude oil

Nutrient solution

Component | Amount
--- | ---
Resazurin | 100 µL
Na$_2$S·9H$_2$O | 0.1 g
NaHCO$_3$ | 1.2 g
Na$_2$MoO$_4$·H$_2$O | 0.01 g
Crude oil | 1 ml
Protein-rich matter | 0.24 g

RELEVANCE OF CO$_2$ SUPPLY IN STIMULATING METHANOGENESIS

- CH$_4$ production only occurred in the microcosm supplied with CO$_2$ as NaHCO$_3$
- The combined supply of protein-rich matter and CO$_2$ promotes the syntrophic growth of a crude oil-degrading microbial community
- High salinity (TDS) levels inhibits the syntrophic growth of a crude oil-degrading microbial community
- The growth of methanogenic microbes was not possible in PW from the Cushing oil field (TDS = 176,665 mg/L)

RELEVANCE OF THE CHEMICAL COMPOSITION OF PRODUCED WATER (PW)

- Although H$_2$ accumulation with PW from the Cushing oil field did occur, this did not result in the production of CH$_4$
- Cushing oil field PW
  - TDS = 176,665 mg/L
- Stillwater oil field PW
  - TDS = 116,714 mg/L

MECHANISM OF METHANOGENIC CRUDE OIL BIODEGRADATION STIMULATION

- The combined supply of protein-rich matter and CO$_2$ promotes the syntrophic growth of a crude oil-degrading microbial community
- High salinity (TDS) levels inhibits the syntrophic growth of a crude oil-degrading microbial community
- The growth of methanogenic microbes was not possible in PW from the Cushing oil field (TDS = 176,665 mg/L)

BENEFICIAL USE OF CO$_2$ AND PW: COUPLING OF CO$_2$ AND PW DISPOSAL?

- a) Mineral trapping of CO$_2$ and heavy metals
- b) Biogenic recycling of CO$_2$ to CH$_4$
- c) Enhanced hydrocarbon recovery
CONCLUSIONS

- Ba mobility is higher in deep saline aquifers than in shallow freshwater aquifers.
- PW contains indigenous methanogenic microbial communities that could be used to recover crude oil in the form of CH₄.
- The combined supply of protein-rich matter and CO₂ stimulates methanogenesis from crude oil and CO₂.
- Coupling of CO₂ and PW disposal into depleted oil reservoirs by the proposed method constitutes an alternative to biogenically recycle CO₂ to CH₄.
- Enhance the recovery of crude oil.
- Trap CO₂ and heavy metals as carbonate minerals.

QUESTIONS?

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- Microbial diversity analysis: Drs. Mostafa Elshahed and Noha Youssef.
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- Crude oil analysis: Mr. Toby Williams (Glimp Oil Co.).

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STIMULATION OF METHANOCENIC CRUDE OIL BIODEGRADATION

- If CH₄ was produced only from the biodegradation of the supplied protein-rich matter, CH₄ production in both microcosms – with and without the crude oil supply – would have been the same (4.0 Vol. %).

Comparison of H₂ and CH₄ gas production in the headspace of microcosms with (1 mL) and without crude oil supply. Both microcosms were supplied with protein-rich matter (2 g).