Method for the Determination of Residual Carbon Dioxide Saturation Using Reactive Ester Tracers

M. Myers, L. Stalker, K.B. Ho, A. Ross and C. Dyt
Senior Researcher with CSIRO and CO2CRC
TCCS-6 Trondheim (June 2011)
Outline

• Why use tracers?
• How tracers have been previously applied to CCS sites
  • Case studies from Frio and Otway
• Inert tracer behaviour
• Reactive tracer behaviour
• Proposed tracers and hydrolysis
• Laboratory determination of partition coefficients
• Computational modelling of reactive tracers vs. inert tracers for residual gas saturation
• Conclusions and ongoing work
  • Single well residual saturation test
    Otway Stage 2B (CO2CRC)
Why use tracers?

- Tracers can:
  - Verify the presence of injected CO$_2$
  - Confirm arrival at monitoring wells/demonstrate breakthrough
  - Show differences in behaviour in different sections of a formation
  - Assurance monitoring
    - overlying aquifers
    - soil gas
    - atmosphere
  - Potentially give information on storage capacity and saturation levels
Case study – Frio Stage 1

- Injection well to monitoring well
- 30 m distance
- 1500 m depth
- Arrival 51 hours

Tracers used:
- Sulphur hexafluoride ($SF_6$)
- Krypton
- Perfluorocarbons
  - perfluoromethylcyclohexane (PMCH)
  - perfluorotr trimethylcyclohexane (PTCH)
  - perfluoromethylcyclobutane (PMCB)
  - perfluorodimethylcyclohexane (PDCH)

From Freifeld et al., 2005
Case Study – Otway

- Injection well to monitoring well
- 300 m distance
- 2000 m depth
- Arrival 101-121 days

Tracers used:
- Sulphur hexafluoride
- Krypton
- Perdeuterated methane
- 1,1,1,2-tetrafluoroethane

Data from Boreham et al., 2011
1. Tracer is injected with water and pushed out of the wellbore into the formation.
2. There it can partition between the water phase (where it is mobile) and the supercritical carbon dioxide phase (where it is stationary).
3. The velocity of the tracer in the formation is therefore dictated by the partition coefficient and the amount of residual CO₂ saturation.
Inert Reactive

= Tracer 1: With higher partitioning coefficient into water ($PC_{H2O}$)

= Parent tracer compound

= Tracer 2: With higher partitioning coefficient into $CO_2$ ($PC_{CO2}$)
Inert Reactive

\[ \text{Tracer 1: } P_{\text{H}_2\text{O}} \]
\[ \text{Tracer 2: } P_{\text{CO}_2} \]

= Parent tracer compound
Reactive tracers require a “soak” time to hydrolyse. Some parent tracer will convert to multiple daughter products.

The daughter products have different functionality to the parent so have different partitioning properties.

- Parent tracer compound
- Daughter hydrolysis compound(s)
Inert Reactive

CSIRO. Determination of Residual Saturation Using Reactive Ester Tracers

\[ \text{Tracer 1: } \text{PC}_{\text{H}2\text{O}} \]

\[ \text{Tracer 2: } \text{PC}_{\text{CO}_2} \]

\[ \text{Hydrolysis compound(s)} \]

\[ \text{Parent tracer compound} \]

\[ \text{Daughter hydrolysis compound(s)} \]
Reactive

CSIRO. Determination of Residual Saturation Using Reactive Ester Tracers

- **Parent tracer compound**
- **Daughter hydrolysis compound(s)**
CSIRO. Determination of Residual Saturation Using Reactive Ester Tracers
Single well test – Inert vs reactive tracers

INERT

\[ = \text{Tracer 1: } PC_{H_2O}\]

\[ = \text{Tracer 2: } PC_{CO_2}\]

REACTIVE

\[ = \text{Parent tracer compound}\]

\[ = \text{Daughter hydrolysis compound(s)}\]
Single well residual saturation test – Otway Stage 2B (CO2CRC)

1. Reactive tracer injected and pushed into formation with CO₂/water.

2. Soak period to allow hydrolysis reaction.

3. Back production and recovery of parent tracer and daughter products.
## Tracers Proposed

<table>
<thead>
<tr>
<th></th>
<th>Triacetin</th>
<th>Tripropionin</th>
<th>Propylene glycol diacetate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td><img src="image" alt="Triacetin Structure" /></td>
<td><img src="image" alt="Tripropionin Structure" /></td>
<td><img src="image" alt="Propylene Glycol Diacetate Structure" /></td>
</tr>
<tr>
<td><strong>Formula</strong></td>
<td>$C_9H_{14}O_6$</td>
<td>$C_{12}H_{20}O_6$</td>
<td>$C_7H_{12}O_4$</td>
</tr>
<tr>
<td><strong>Breakdown/daughter products</strong></td>
<td>Glycerol</td>
<td>Glycerol</td>
<td>Propylene glycol</td>
</tr>
<tr>
<td></td>
<td>Partially hydrolysed triacetin</td>
<td>Partially hydrolysed tripropionin</td>
<td>Partially hydrolysed propylene glycol diacetate</td>
</tr>
<tr>
<td></td>
<td>Acetic acid</td>
<td>Propionic acid</td>
<td>Acetic acid</td>
</tr>
<tr>
<td><strong>Partitioning coefficient</strong></td>
<td>~10</td>
<td>~50</td>
<td>~4</td>
</tr>
<tr>
<td><strong>Cost per Kg</strong></td>
<td>$3$</td>
<td>$8$</td>
<td>$10$</td>
</tr>
<tr>
<td><strong>OHSE on parent and daughter compounds</strong></td>
<td>Parent compounds are commonly used as food flavourings and cosmetic additives. The corresponding acids and alcohols (hydrolysis daughter products) are also food and cosmetic additives.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Amounts required</strong></td>
<td>Solubility = 72g/L</td>
<td>Solubility = 2.6g/L</td>
<td>Solubility = 100g/L</td>
</tr>
</tbody>
</table>

*CSIRO. Determination of Residual Saturation Using Reactive Ester Tracers*
Summary of what we expect to see

- **Non-reactive no drift PC 5**
- **Non-reactive no drift PC 0.2**

**Legend:**
- Red = With higher partitioning coefficient into CO₂
- Green = With higher partitioning coefficient into H₂O

**Graph:**
- Y-axis: Relative abundance
- X-axis: Hours
- CO₂ saturation = 0.2

**Diagrams:**
- Tracers injected
- Tracers produced

CSIRO. Determination of Residual Saturation Using Reactive Ester Tracers
Summary of what we expect to see

- With higher partitioning coefficient into CO₂
- With higher partitioning coefficient into H₂O

**CO₂ saturation = 0.2**

**Drift**

Tracers injected

Tracers produced

CSIRO. Determination of Residual Saturation Using Reactive Ester Tracers
Summary of what we expect to see

- **Inert tracers**
  - No drift velocity
  - 1.08 m/day drift velocity

- **Reactive tracers**
  - No drift velocity
  - 1.08 m/day drift velocity

- For each set of conditions, there are plots showing the concentration over time.
Conclusions & Ongoing work

• Conclusions
  • Reactive tracers are potentially more accurate and robust systems for determining residual saturation (including drift) compared to inert tracers
  • Choice of reactive tracer is dictated by
    • Residual saturation estimation
    • Temperature (reaction kinetics)
    • pH & salinity
    • Rock matrix (adsorption effects)
    • Toxicity

• Ongoing work
  • Field trials at CO2CRC Otway Residual Saturation Test
  • Analytical method development
  • Laboratory experiments to develop a package of partition coefficients and core flood experiments