Effects of Impurities on Geological Storage of Carbon Dioxide

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Study Partners

- Study was commissioned by GCCSI and IEAGHG and carried out by NRCan

Jinsheng Wang, David Ryan, Edward J. Anthony, Andrew Wigston, CanmetENERGY, Natural Resources Canada
Study Background

Flue Stream Composition determined by:
- Feedstock
- Combustion process/technology
- Capture technology employed
- Operating Conditions
Study Objective

- To evaluate the physical and chemical effects of impurities in the injected flue stream on the storage operation

Physical Properties of impure CO₂ stream

- Phase behaviour
- Density
- Viscosity
- Buoyancy
- Solubility

Impact on injection and storage

- Storage capacity
- Injectivity
- Trapping mechanisms
- Caprock + Wellbore integrity

Geochemical Reaction Potential

- Precipitation/Dissolution

Scenarios
# Stream Compositions

<table>
<thead>
<tr>
<th>Component</th>
<th>Pre-combustion</th>
<th>Post-combustion</th>
<th>Oxyfuel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Selexol</td>
<td>Rectisol</td>
<td>Comp. 1</td>
</tr>
<tr>
<td>$\text{CO}_2$ (vol %)</td>
<td>97.95</td>
<td>99.7</td>
<td>99.93</td>
</tr>
<tr>
<td>$\text{O}_2$ (vol %)</td>
<td>-</td>
<td>-</td>
<td>0.015</td>
</tr>
<tr>
<td>$\text{N}_2$ (vol %)</td>
<td>0.9</td>
<td>0.21</td>
<td>0.045*</td>
</tr>
<tr>
<td>Ar (vol %)</td>
<td>0.03</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>$\text{NO}_x$ (ppm)</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>$\text{SO}_2$ (ppm)</td>
<td>-</td>
<td>-</td>
<td>10$^{\dagger}$</td>
</tr>
<tr>
<td>$\text{SO}_3$ (ppm)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Physical Effects

- Effects of non-condensables – $N_2$, $O_2$, $Ar$
  - Lower critical temperatures
    - Increase bubble-point pressure
    - Decrease critical temperature
  - Reduce Density
  - Reduce Viscosity
Phase Behaviour

Non-condensable impurities (N₂, O₂, Ar) affect:

- bubble-point pressure;
- critical T. and density;
- viscosity
Storage Capacity

Normalised Storage Capacity

\[ \frac{M}{M_0} = \frac{\bar{\rho}}{\rho_0 (1 + \sum_i \frac{m_i}{m_{CO2}})} \]

For all mixtures of supercritical CO₂ and non-condensable gases, there is a **maximum decrease** of the storage capacity at a certain pressure under a given temperature.

Increasing temperature will shift the maximum decrease to a higher pressure and its magnitude decreases.
## Capacity Scenarios for high impurity stream

<table>
<thead>
<tr>
<th>Cases</th>
<th>Depth (m)</th>
<th>P (MPa)</th>
<th>T (° C)</th>
<th>T grad (° C/m)</th>
<th>Storage Capacity (kg CO₂/m³ pore)</th>
<th>Fᵇ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pure</td>
<td>Impure</td>
</tr>
<tr>
<td>Shallow-Low Temp</td>
<td>895</td>
<td>9.2</td>
<td>33</td>
<td>0.020</td>
<td>647.68</td>
<td>253.96</td>
</tr>
<tr>
<td>Shallow-Mid Temp</td>
<td>895</td>
<td>9.2</td>
<td>38</td>
<td>0.025</td>
<td>540.97</td>
<td>231.20</td>
</tr>
<tr>
<td>Shallow-High Temp</td>
<td>895</td>
<td>9.2</td>
<td>45</td>
<td>0.033</td>
<td>364.48</td>
<td>208.72</td>
</tr>
<tr>
<td>Median-Low Temp</td>
<td>2338</td>
<td>24</td>
<td>62</td>
<td>0.020</td>
<td>750.04</td>
<td>550.35</td>
</tr>
<tr>
<td>Median-Mid Temp</td>
<td>2338</td>
<td>24</td>
<td>75</td>
<td>0.025</td>
<td>675.00</td>
<td>493.67</td>
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<tr>
<td>Median-High Temp</td>
<td>2338</td>
<td>24</td>
<td>92</td>
<td>0.033</td>
<td>584.92</td>
<td>432.23</td>
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<tr>
<td>Deep-Low Temp</td>
<td>3802</td>
<td>38.8</td>
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<td>611.13</td>
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<tr>
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<td>113</td>
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<td>551.25</td>
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<tr>
<td>Deep-High Temp</td>
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<td>38.8</td>
<td>141</td>
<td>0.033</td>
<td>611.35</td>
<td>485.19</td>
</tr>
</tbody>
</table>
### Physical Effects - Injectivity

The equation for Normalised Permeation Flux is given by:

\[
\frac{\dot{M}_{CO_2}}{\dot{M}_0} = \frac{\rho (\mu_0 / \mu)}{\rho_0 (1 + \sum m_i / m_0)}
\]

<table>
<thead>
<tr>
<th>Cases</th>
<th>Depth (m)</th>
<th>P (MPa)</th>
<th>T (°C)</th>
<th>T grad (°C/m)</th>
<th>Viscosity(^a) (-)</th>
<th>Injectivity(^b) (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shallow-Low Temp</td>
<td>895</td>
<td>9.2</td>
<td>33</td>
<td>0.020</td>
<td>0.38</td>
<td>1.0</td>
</tr>
<tr>
<td>Shallow-Mid Temp</td>
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<td>9.2</td>
<td>38</td>
<td>0.025</td>
<td>0.45</td>
<td>0.94</td>
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<tr>
<td>Shallow-High Temp</td>
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<td>9.2</td>
<td>45</td>
<td>0.033</td>
<td>0.77</td>
<td>0.74</td>
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<tr>
<td>Median-Low Temp</td>
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<td>24</td>
<td>62</td>
<td>0.020</td>
<td>0.72</td>
<td>1.0</td>
</tr>
<tr>
<td>Median-Mid Temp</td>
<td>2338</td>
<td>24</td>
<td>75</td>
<td>0.025</td>
<td>0.75</td>
<td>0.98</td>
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<tr>
<td>Median-High Temp</td>
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<td>92</td>
<td>0.033</td>
<td>0.79</td>
<td>0.93</td>
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<tr>
<td>Deep-Low Temp</td>
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<td>0.020</td>
<td>0.81</td>
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<tr>
<td>Deep-Mid Temp</td>
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<td>0.83</td>
<td>0.95</td>
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<tr>
<td>Deep-High Temp</td>
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<td>38.8</td>
<td>141</td>
<td>0.033</td>
<td>0.87</td>
<td>0.91</td>
</tr>
</tbody>
</table>
Effects on Buoyancy

- Density decrease → increased buoyancy
- Increased buoyancy → Increased rising velocity
- Base case 15% light impurities, buoyancy increased by up to 50% (depending on temperature and pressure) - increase the rising velocity of injected CO$_2$ plume up to 3 times.
- Potential to reduce residual trapping and increase lateral spreading of plume at the caprock (dependent on reservoir heterogeneity)
Normalized buoyancy for Oxy-1 Stream at 330 K

Effects on solubility trapping:
Less contact with brine = less solubility trapping
Chemical Effects

- Most significant species - $\text{SO}_x$, $\text{NO}_x$, H$_2$S.
- Impact of Reactive Impurities on Capacity and Injectivity
  - Formation of sulphuric acid
    - $\text{NO}_x$ catalyses oxidation of $\text{SO}_2$ to form sulphuric acid – lowers pH
    - Dissolution and Precipitation, eg $\text{CaCO}_3 \rightarrow \text{CaSO}_4$
  - Effect of dry-out zone
  - Potential deposition of sulphur if co-injection of H$_2$S and SO$_2$
Effects on Caprocks and Well Materials

- Caprocks
  - $\text{SO}_x$ and $\text{NO}_x \rightarrow$ sulphuric and nitric acid
  - If 1.5% $\text{SO}_x$ and $\text{NO}_x$ – dissolution 50%
  - But expected conc. < 200ppm – dissolution insignificant
  - Possible impact of $\text{O}_2$ – only if large quantities

- Well Materials
  - Post-injection – return of water with acidic impurities
  - Can cause dissolution of cement/ steel casings
  - Cement/ casing quality need to be improved
Conclusions

• Physical Effects – non-condensable \( N_2, O_2, Ar \)
  • Storage Capacity reduction – most significant
  • \( SO_2 \) can increase capacity – not significant
  • Decrease of injectivity
  • Decrease of solubility trapping

• Chemical Effects
  • \( NO_x \) can promote oxidation of \( SO_2 \) to sulphuric acid
  • Impact of \( SO_2 \) on porosity/ injectivity – less than previously believed because of dry-out zone
  • \( H_2S \) and \( SO_2 \) co-injected – potential deposition of sulphur
  • Caprock dissolution insignificant, \( NO_x, SO_2 < 200ppm \)
  • Possible adverse effect on well materials – need higher quality materials
Thank you

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