Ocean & Geologic Sequestration of CO$_2$ with Particle Stabilized Emulsions for GHG Mitigation

Dr. David K. Ryan
Department of Chemistry
University of Massachusetts Lowell

&

Intercampus Marine Sciences Graduate Program
University of Massachusetts

http://faculty.uml.edu/David_Ryan
Acknowledgements

- Coworkers
  - Drs. Dan Golomb, Eugene Barry, Steve Pennell
  - Students Peter Swett, Mike Woods, Huishan Duan, Jon Hedges

- Funding
  - U.S. Department of Energy
  - Mass. Technology Transfer Center (MTTC)
  - ARRA
The Problem
Atmospheric CO₂ Levels on the Rise

Atmospheric Carbon Dioxide
Measured at Mauna Loa, Hawaii

Source: Keeling et al.
The Greenhouse Effect

Some solar radiation is reflected by the Earth and the atmosphere.

Some of the infrared radiation passes through the atmosphere, and some is absorbed and re-emitted in all directions by greenhouse gas molecules. The effect of this is to warm the Earth's surface and the lower atmosphere.

Solar radiation passes through the clear atmosphere.

Most radiation is absorbed by the Earth's surface and warms it.

Infrared radiation is emitted from the Earth's surface.

Source: OSTP

(Without greenhouse average earth temp. ~ -25°C instead of +15°C with)
The Answer

Or at least one answer
CO$_2$ Sequestration

- Storing or permanently immobilizing CO$_2$ in some form to remove it from the atmosphere or prevent it from entering the atmosphere

- General schemes include
  - Capture and store
    - In geologic formations
    - In the deep ocean
  - Converting to Biomass (terrestrial or oceanic e.g. IRONEX program for ocean fertilization)
CO₂ Emissions Can Be Reduced By Several Means (other answers)

- Conservation and efficiency improvements
- Substitute high carbon fuels (i.e. coal) with low carbon fuels (i.e. natural gas)
- Renewable energies
  1. Wind
  2. Solar  (UMass Lowell Team – Solar Decathlon)
  3. Biomass
  4. Geothermal
  5. Ocean thermal, ocean tides, ocean waves
- Nuclear energy
### CO₂ Emissions By Sector

**USA 2016**

<table>
<thead>
<tr>
<th>Sector</th>
<th>Mt CO₂/y</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric power plants</td>
<td>1821</td>
<td>26</td>
</tr>
<tr>
<td>Industrial</td>
<td>1388</td>
<td>20</td>
</tr>
<tr>
<td>Transportation</td>
<td>1883</td>
<td>27</td>
</tr>
<tr>
<td>Residential</td>
<td>998</td>
<td>14</td>
</tr>
<tr>
<td>Commercial</td>
<td>902</td>
<td>13</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>6992</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Source: U.S. Energy Information Administration, April 2017
## Global Emissions of CO$_2$ for Large Stationary Sources

<table>
<thead>
<tr>
<th>Process</th>
<th>No. of sources</th>
<th>Emissions (MtCO$_2$/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fossil Fuels</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power (coal, gas, oil and others)</td>
<td>4,942</td>
<td>10,539</td>
</tr>
<tr>
<td>Cement production</td>
<td>1,175</td>
<td>932</td>
</tr>
<tr>
<td>Refineries</td>
<td>638</td>
<td>798</td>
</tr>
<tr>
<td>Iron and steel industry</td>
<td>269</td>
<td>646</td>
</tr>
<tr>
<td>Petrochemical industry</td>
<td>470</td>
<td>379</td>
</tr>
<tr>
<td>Oil and gas processing</td>
<td>N/A</td>
<td>50</td>
</tr>
<tr>
<td>Other sources</td>
<td>90</td>
<td>33</td>
</tr>
<tr>
<td><strong>Biomass</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioethanol and bioenergy</td>
<td>303</td>
<td>91</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>7,887</strong></td>
<td><strong>13,466</strong></td>
</tr>
</tbody>
</table>
How it Works
Ways of capturing CO₂ before it is released to the atmosphere:

- Chemical absorption
- Physical adsorption
- Coal gasification with physical adsorption
- Oxyfuel combustion
Overview of CO₂ Capture Schemes

Post combustion

Pre combustion

Oxyfuel

Industrial processes

Coal Gas Biomass

Power & Heat

CO₂ Separation

N₂ O₂

CO₂

Gasification

Reformer +CO₂ Sep.

H₂

Power & Heat

N₂ O₂

N₂

Air Separation

Air

O₂

CO₂

Process +CO₂ Sep.

Raw material

Gas, Ammonia, Steel
CO₂ Capture Technologies

Ways of capturing CO₂ before it is released to the atmosphere:

- Chemical absorption
- Physical adsorption
- Coal gasification with physical adsorption
- Oxyfuel combustion

\[
3\text{C (i.e., coal)} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2 + 3\text{CO}
\]

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{energy}
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\]

\[
2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O(g)} + \text{heat}
\]
Then What?

$\text{CO}_2$ Sequestration
Ocean sequestration options

Dispersal of CO$_2$ by ship
Dispersal of CO$_2$/CaCO$_3$ mixture
Refilling ship
Rising CO$_2$ plume
Sinking CO$_2$ plume
CO$_2$ lake
CO$_2$ lake
Flue gas
Captured and compressed CO$_2$

Source: IPCC Special Report on CC&S, 2005
Problems with Scenarios for Ocean Sequestration of CO$_2$

- **High Costs** - exclusive of capture
- **Proximity of Sources to Ocean**
- **Ecological Effects**
  - Physical Impact of Immiscible Liquid
  - Chemical Impacts
    - pH
    - Carbonate hot spots
- **Long Term Uncertainty**
  - Chemical Effects
  - Lake Nyos Syndrome
- **London Convention 1972**
Our Discovery

In 2001 we discovered how to make emulsions of liquid CO$_2$ and water stabilized by fine particles.
Some simple chemistry

- Immiscible liquids form two layers with an **interfacial tension** or force between them.
Applying shear force or mixing creates a dispersion

Droplets of a dispersion quickly coalesce to larger & larger drops resulting in two layers once again
Emulsions

- When an **emulsifying agent** is added to a two phase system, interfacial tension is greatly reduced allowing formation of **stable** dispersions or emulsions.

- Emulsions can be either **macroemulsions** or **microemulsions** depending on droplet size.
Particle Stabilized Emulsions (also called Pickering Emulsions)

- Very fine particles can act as emulsifying agents, though more common emulsifiers are surfactants like soaps and detergents.
- Emulsifying agents work by arranging themselves at the interface between liquids.
Particle Stabilized Emulsions

Immiscible liquids form an emulsion with fine particles. System: dodecane (top), water, calcite and iodine for color.
Particle Stabilized Emulsions

- **Hydrophilic particles** form oil-in-water emulsions:
  - Calcite (CaCO$_3$)
  - Pulverized sand (SiO$_2$)
  - Lizardite & other minerals

- **Hydrophobic particles** form water-in-oil emulsions:
  - Carbon black
  - Pulverized coal
  - Teflon particles
Liquid CO$_2$/Seawater/CaCO$_3$ Macroemulsion (a.k.a. Globulsion)

~200 µm droplets (globules)
The Grand Finale
Calcite Stabilized CO$_2$ Emulsion sinks as a dense plume several hundred meters until it equilibrates with stratified seawater.

CO$_2$ Emulsion globules ‘rain out’ toward bottom.

Diagram by P. Swett, Animation by N.C.Y. Lee
Ocean Sequestration of Carbon Dioxide: Modeling the Deep Ocean Release of a Dense Emulsion of Liquid CO₂-in-Water Stabilized by Pulverized Limestone Particles

D. Golomb,* S. Pennell, D. Ryan, E. Barry, and P. Swett

Departments of Environmental, Earth and Atmospheric Sciences, Mathematical Sciences, Chemistry, and Chemical Engineering, University of Massachusetts Lowell, Massachusetts 01854

See also Environ. Sci. Technol. 2004, 38, 4445-4450
What Next?
Inverted Emulsions

Water-in-Liquid CO$_2$ (W/C) emulsion stabilized by pulverized coal particles. 70% CO$_2$(l)/30% H$_2$O(l), 2% pulverized coal, 4 μm mean particle diameter.
Dodecane/Water/Carbon Black Microemulsion (10-20 μm) for EOR

Dodecane

Carbon Black Coated Water Droplets
EOR with Particle Stabilized Emulsions of CO₂ & Water

- **Injection Well**
- **Production Well**
- **Emulsion System**
- **Separation & Storage**
  - Oil, Gas, Water

**Diagram Notes:**
- **Carbon Dioxide**
- **Emulsion Flood**
- **Stranded Crude Oil**
Production

Primary
Simple Pumping

Secondary
Water Flooding

Tertiary
EOR
Sinking Crude Oil Emulsion

Crude Oil (slick) on Seawater

Before Emulsion Formation
Crude Oil on Seawater

Dense Crude Oil Emulsion with Calcite

Dense Crude Oil Emulsion sinks in seawater