Emerging Applications of Gas Hydrates

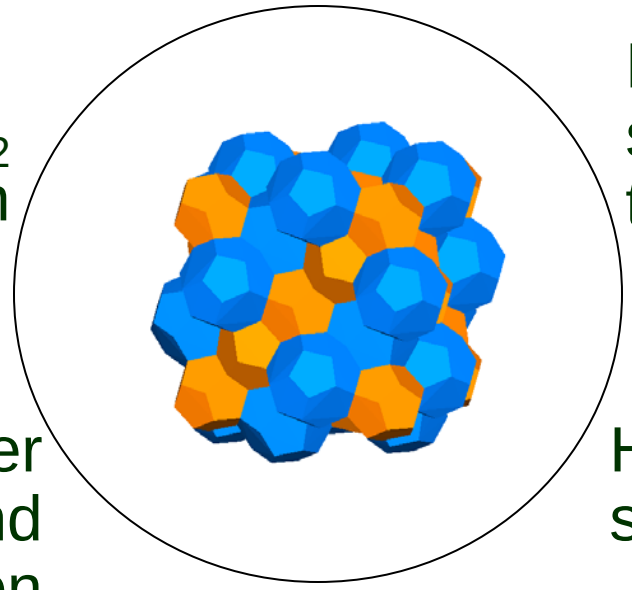
C. Tsouris

Oak Ridge National Laboratory

tsourisc@ornl.gov

Why We Are Interested?

Several Applications of Gas Hydrates Are Currently Investigated



Natural gas production

Natural gas storage and transportation

Hydrogen storage

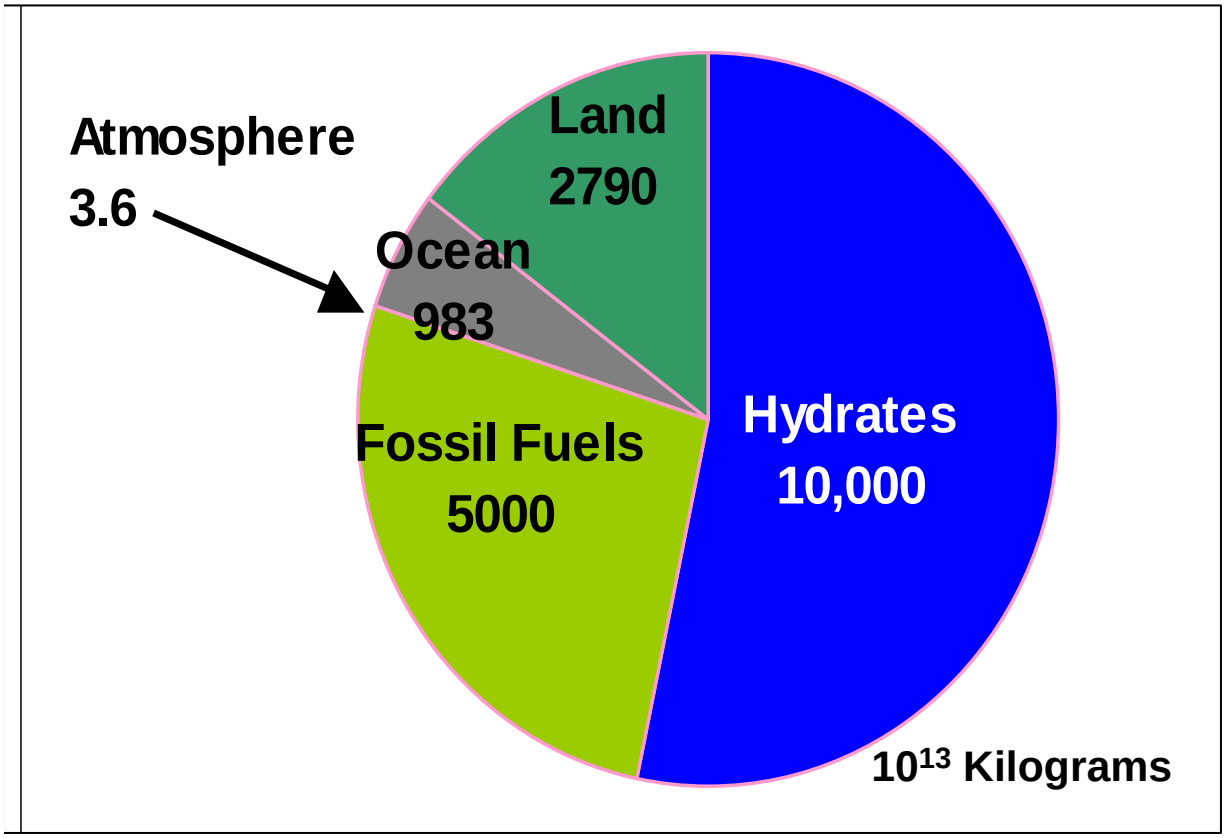
Gas separation

Water treatment and desalination

CO_2 sequestration

Natural Gas Hydrate

Distribution of Global Organic Carbon



Globally distributed in ocean sediments 500-1500 meters below sea surface

> 99% of gas trapped in hydrate is methane

Recent estimates
Kvenvolden, 1999

Ocean Sediments	Permafrost Sediments
20-40 X 10^{15} m^3	1 X 10^{15} m^3

Natural Gas Hydrate as Energy Source

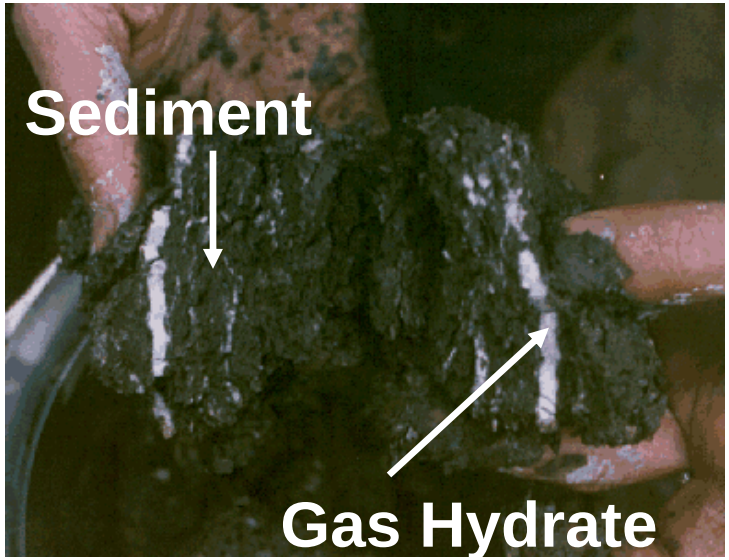
Natural Gas is the least environmentally destructive fossil fuel

Increasing demand (50% by 2025)[1]
Decreasing supply (58 yrs at current use levels)[2]

Natural gas hydrate is a potentially vast future natural gas source

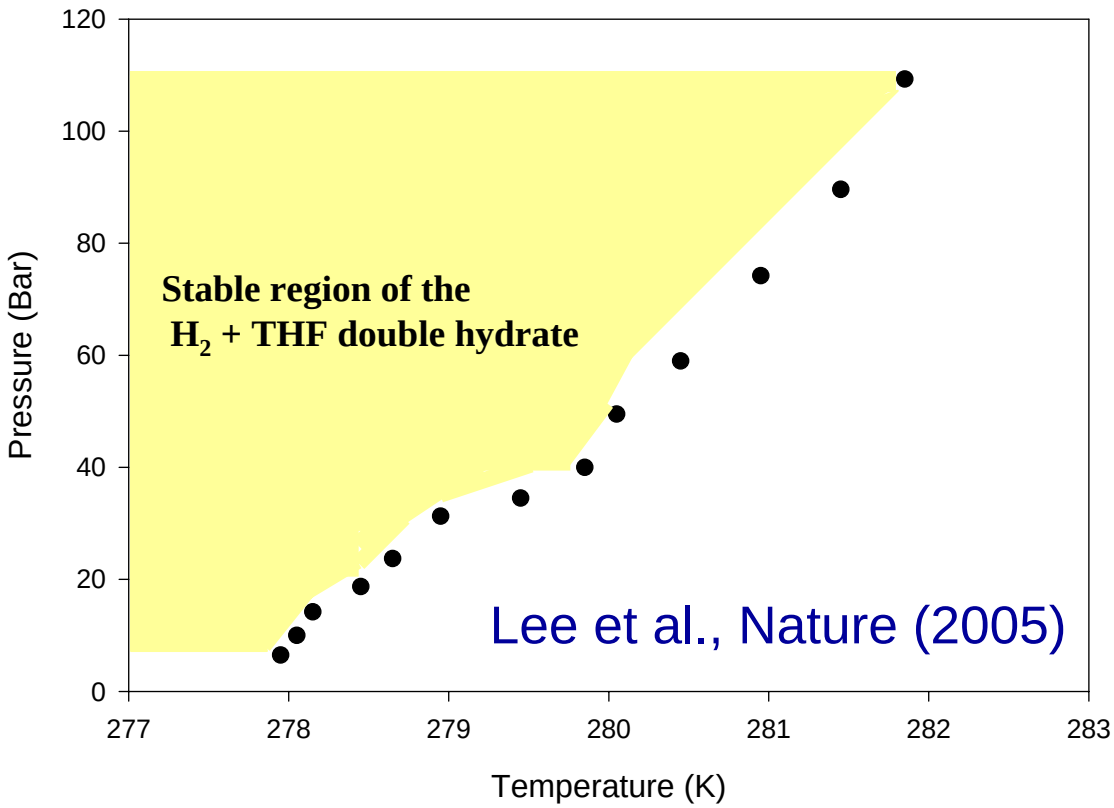
The question is how to extract methane from the hydrate

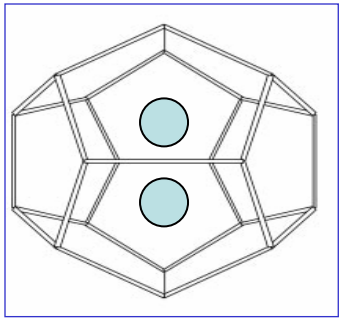
Hydrate formation is also investigated for the purpose of natural gas storage and transport

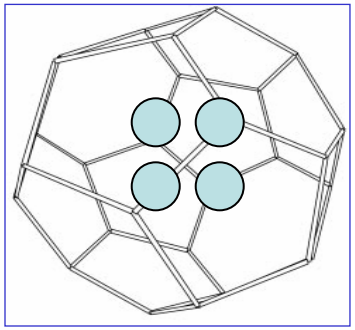


[1] API
[2] USGS

Hydrogen Hydrate







Hydrate formation using pure hydrogen and water requires extreme thermodynamic conditions that make it impractical

Addition of small amounts of THF has been shown to decrease the pressure of the stability region

Gas Separation Through Hydrate Formation and Dissociation

Principle: For a gas mixture containing a hydrate-forming component, hydrate formation may be used for gas separation

Method has been proposed for the separation of CO_2 from flue gas. A $15 M project is supported by Fossil Energy to demonstrate this process.

Produced H_2O Treatment[1]

- Problems with Produced Water:
  - Oil production yields environmentally hazardous H_2O
  - Transport of produced water is expensive
- Benefit of Hydrate Treatment:
  - Treated water can be used for agricultural purposes and possibly as a potable source
  - Treatment at well head eliminates transport

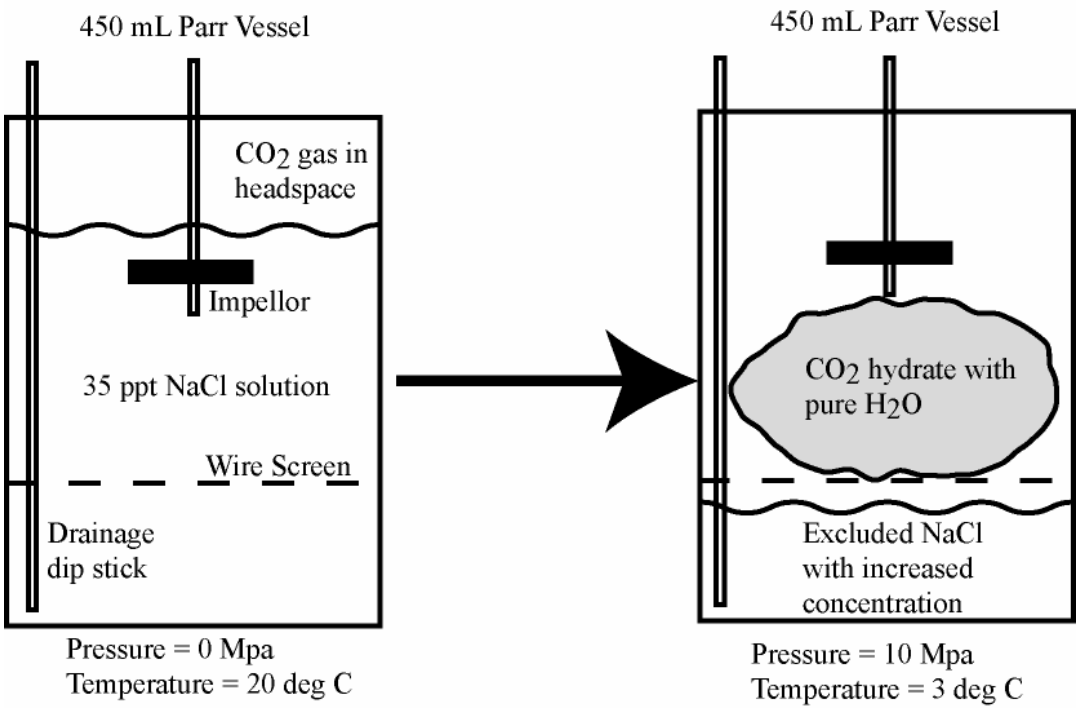
[1]New project between ORNL and BC Technologies (Wyoming)

Process of Treatment

- Controlled formation of hydrates purifies H_2O
- Specific crystalline structure of hydrates excludes impurities
- Hydrate separated from excluded H_2O is thawed to yield purified H_2O
- Kinetics can be increased by adding nucleating agents (e.g., Snomax®) and specific gases (e.g., propane or butane)

Preliminary Results

- Hydrate treatment of H_2O with starting salinity of 35 ppt
- Treated H_2O salinity shown in red
- Experiments conducted by forming hydrate in a 450 mL vessel filled with ~400 mL of 3.5% salt water
- Hydrate was separated from the excluded saline water and then thawed
- The salinity of the thawed water was significantly reduced



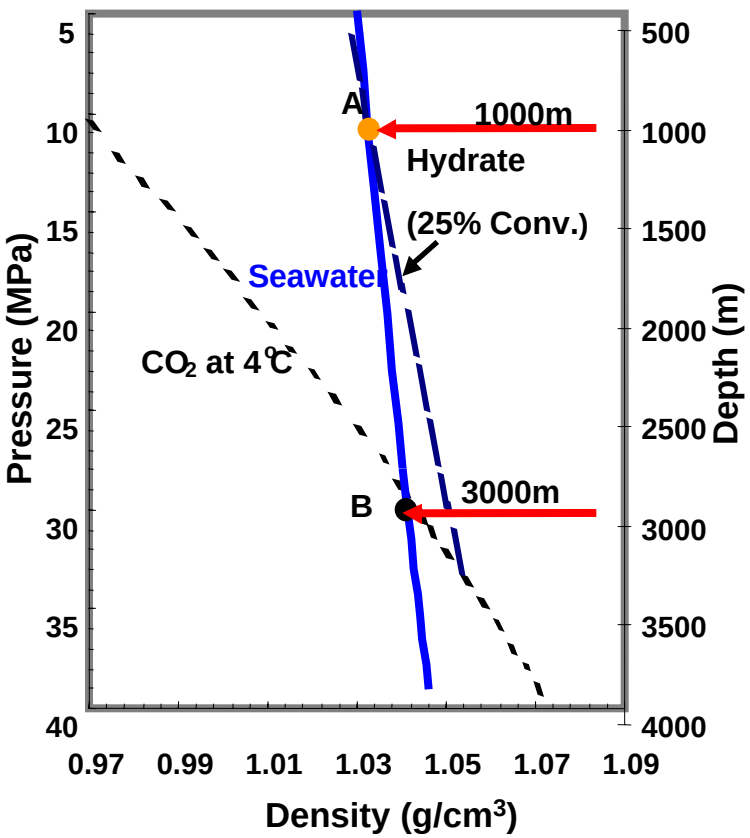
	Starting Salinity (ppt)	**Final Salinity (ppt)**
Expt. 1	35	**9**
*Expt. 2	35	**5**
*Expt. 3	35	**2**

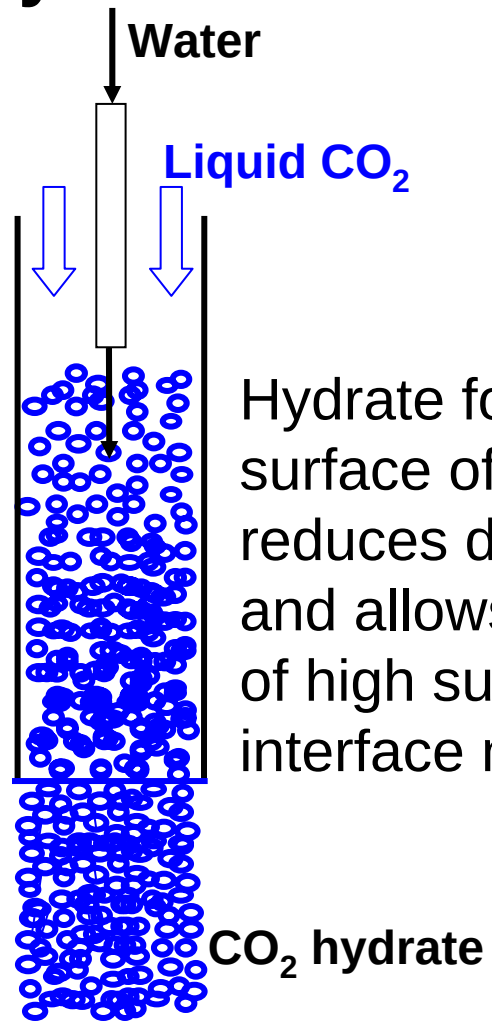
* nucleating agent used

CO2 Sequestration

Concept for CO_2 Hydrate Formation

Pressure/Depth versus Density



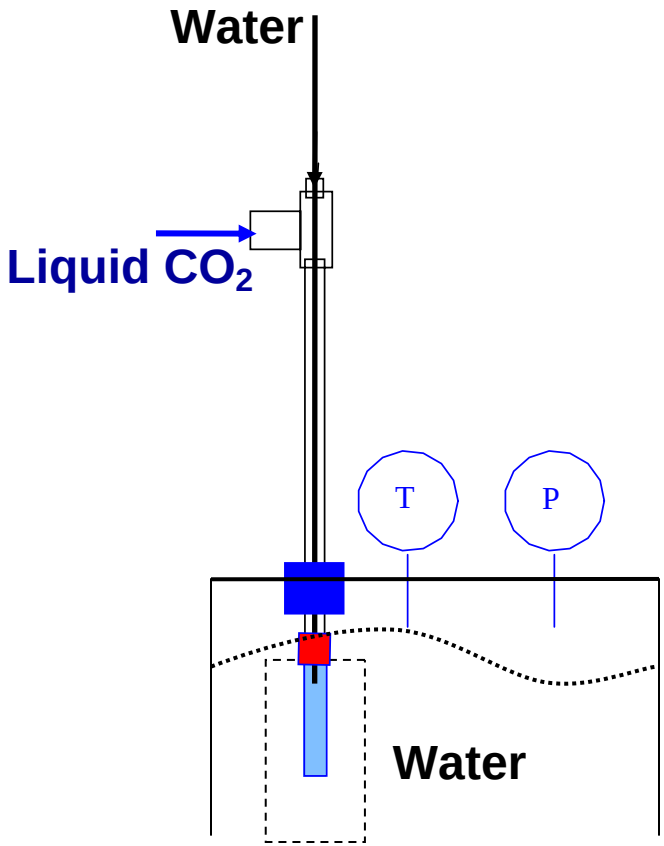


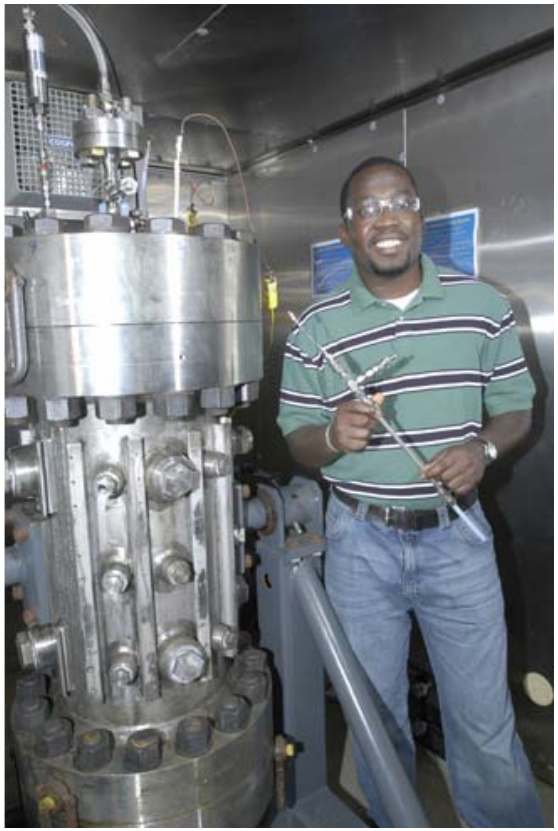
Hydrate formation on the surface of droplets reduces drop coalescence and allows the formation of high surface area for interface mass transfer

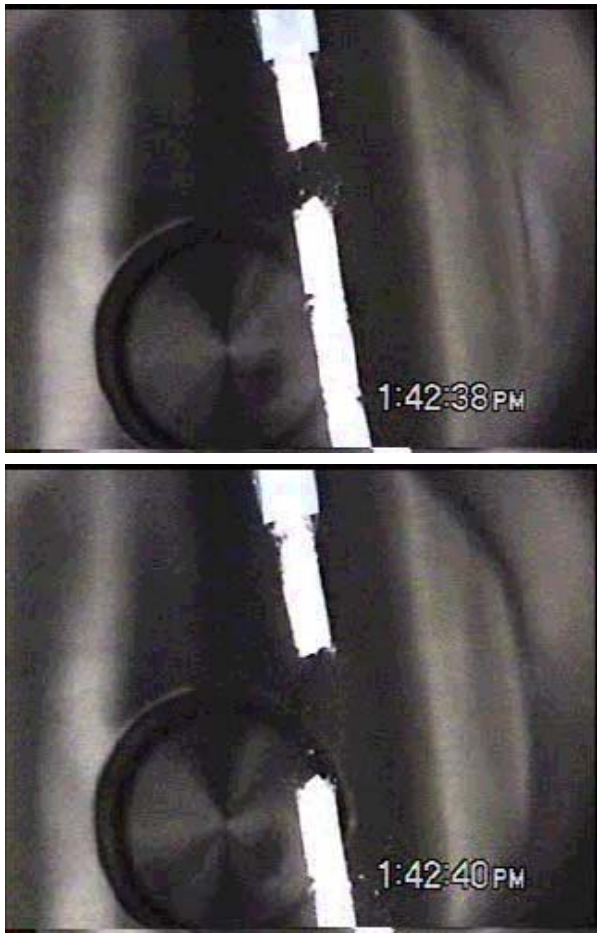
The density of the solid produced depends highly on the conversion of liquid CO_2 to hydrate.

West et al., AIChE J., 2003

The Continuous-Jet Hydrate Reactor Contacts Two Fluids to Form a Solid





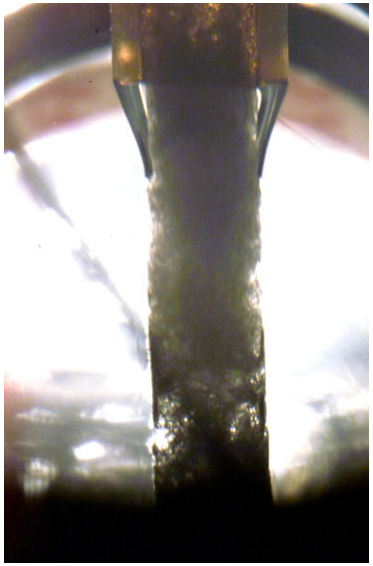


(72-L high pressure vessel)

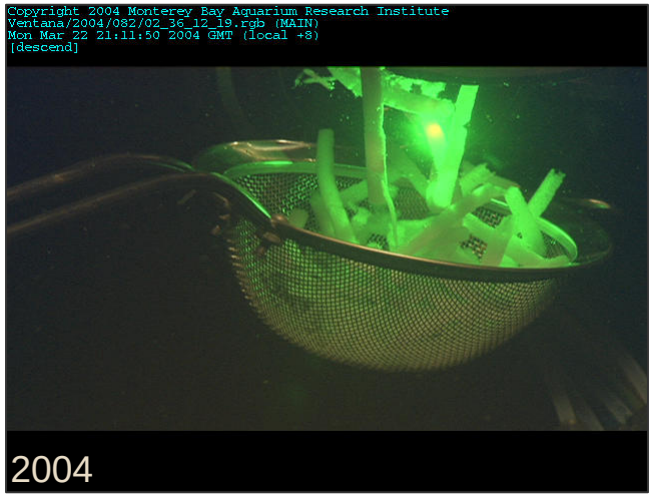
Formation of dense CO_2 hydrate composite was demonstrated in the laboratory using the CJHR reactor.

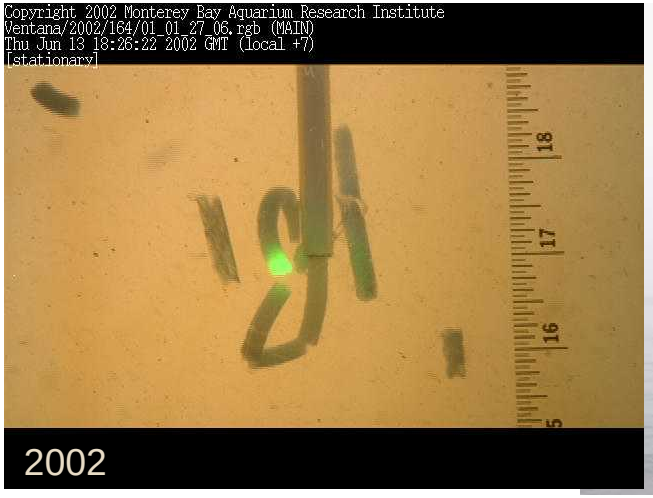
Lee et al., ES&T, 2003

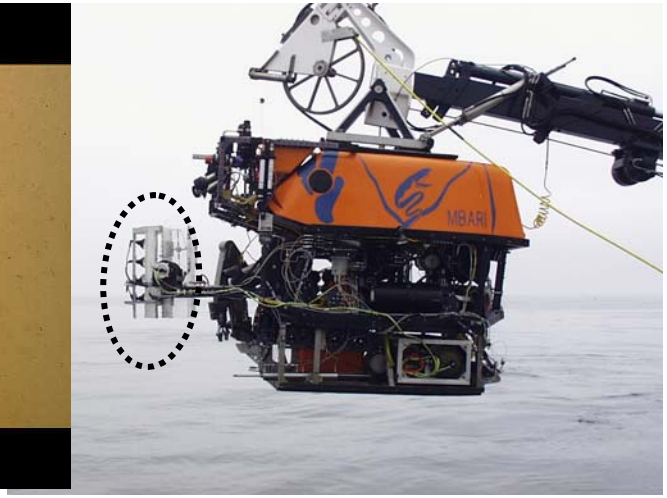
From the Laboratory to the Field



(Installation of ORNL injector with Raman spectrometer)

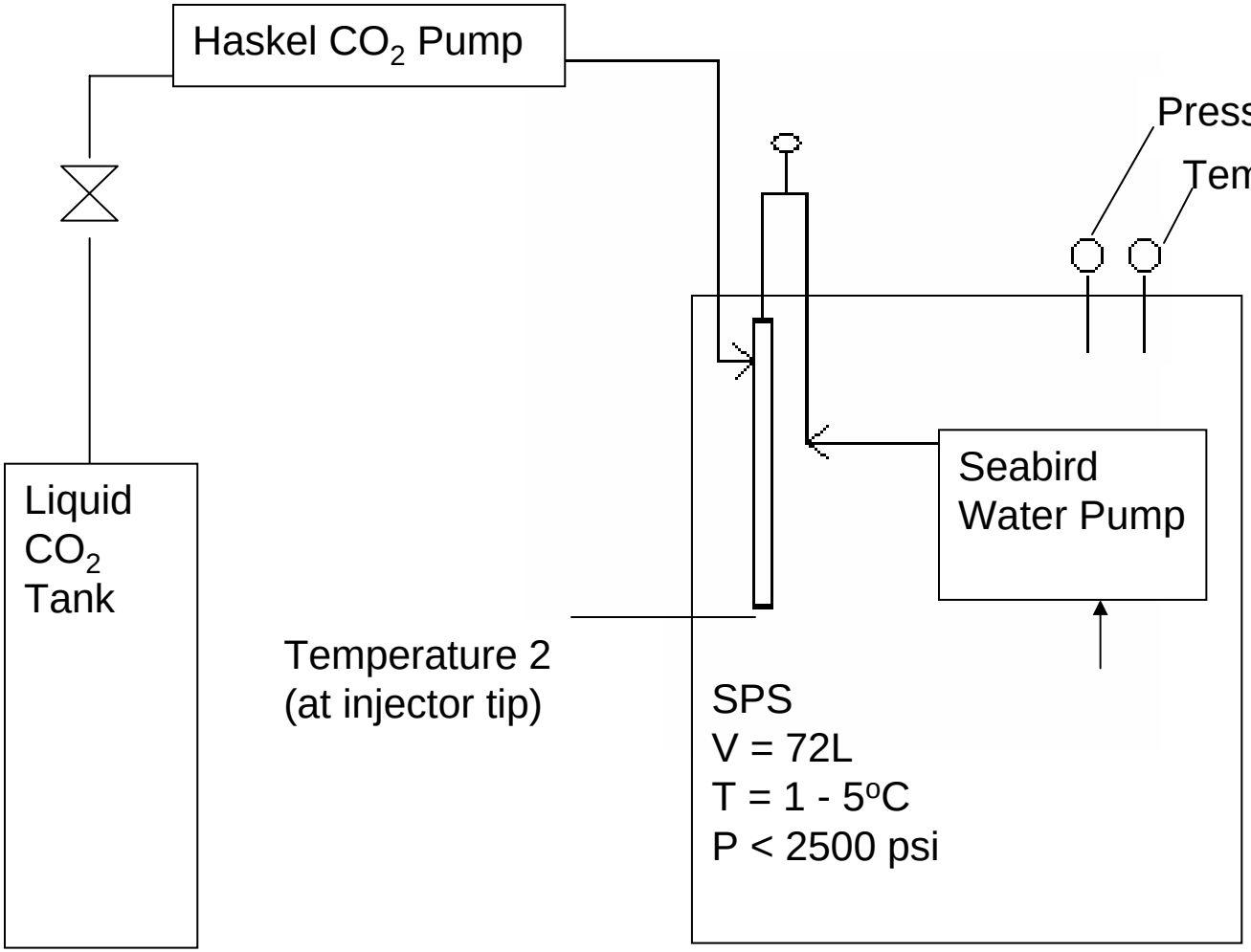






Tsouris et al., ES&T, 2004; Riestenberg et al., ES&T, 2005

Experimental Setup for Scale-up Studies



The experimental setup for the scale-up experiments included a submersible water pump operating at a high pressure and an externally mounted pulsed CO_2 pump.

Summary and Conclusions

- **Research on gas hydrates has been driven mainly for energy production**
- **Natural gas and hydrogen hydrates can be used for safe storage and transportation of natural gas and hydrogen**
- **Gas hydrates can be used for gas separations**
- **Produced water may be treated by formation and dissociation of gas hydrates**
- **CO_2 hydrate can be used in ocean carbon sequestration**

Collaborators

Carbon Sequestration

Liyuan Liang, Libby West, David Riestenberg, Scott McCallum, Phillip Szymcek, Patricia Taboada Serrano, Monsuru Gborigi, Michael Lance, Jorge Gabitto, Sangyong Lee (ORNL)

Peter Brewer, Edward Peltzer, Peter Walz (MBARI)

Eric Adams, Aaron Chow (MIT)

Robert Warzinski (NETL)

Produced Water Treatment

Tommy Phelps, Tony Palumbo, Scott McCallum, Phillip Szymcek, Megan Elwood Madden (ORNL)

John Boysen (BC Technologies)