Field Studies of CO_2/Water Coflow Injection for Ocean Carbon Sequestration

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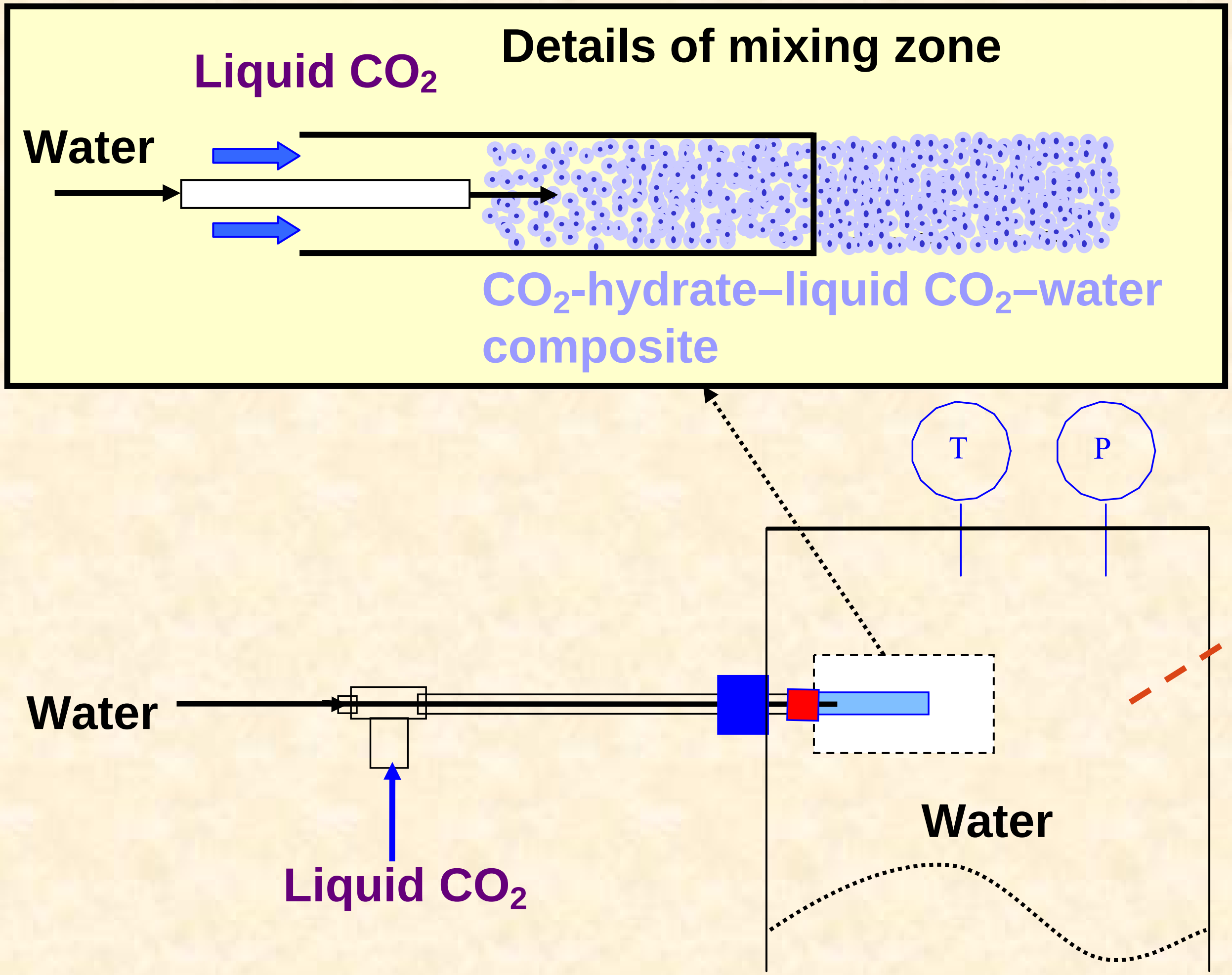
Introduction

- Sinking CO_2 hydrate composite particles have been produced in the laboratory at pressures equivalent to ocean depths of 1000-1300 m.
- Field tests of a CO_2/water coflow injector were conducted in Monterey Bay, CA, in 2002 and 2004 at depths of 1000-1300m.
- The objective was to demonstrate the continuous production of a sinking phase of CO_2 at intermediate ocean depths and observe its dissolution rate.
- A CO_2 hydrate dissolution model suggests that mass transfer through the hydrate layer is the rate limiting step.

The Continuous-Jet Hydrate Reactor

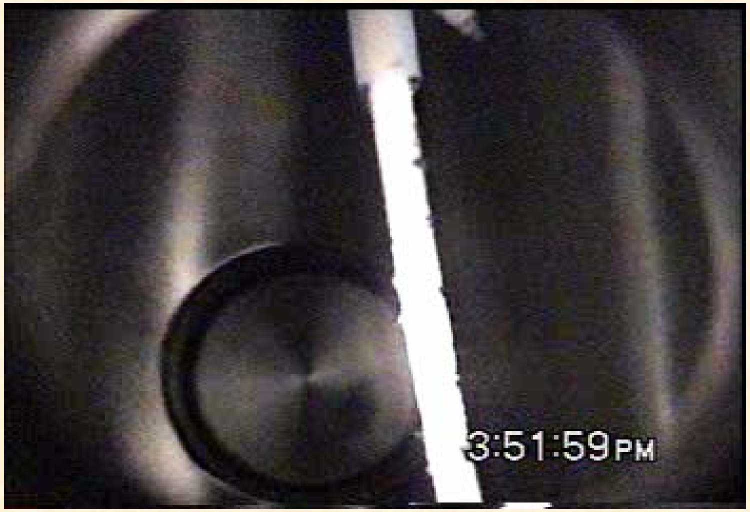


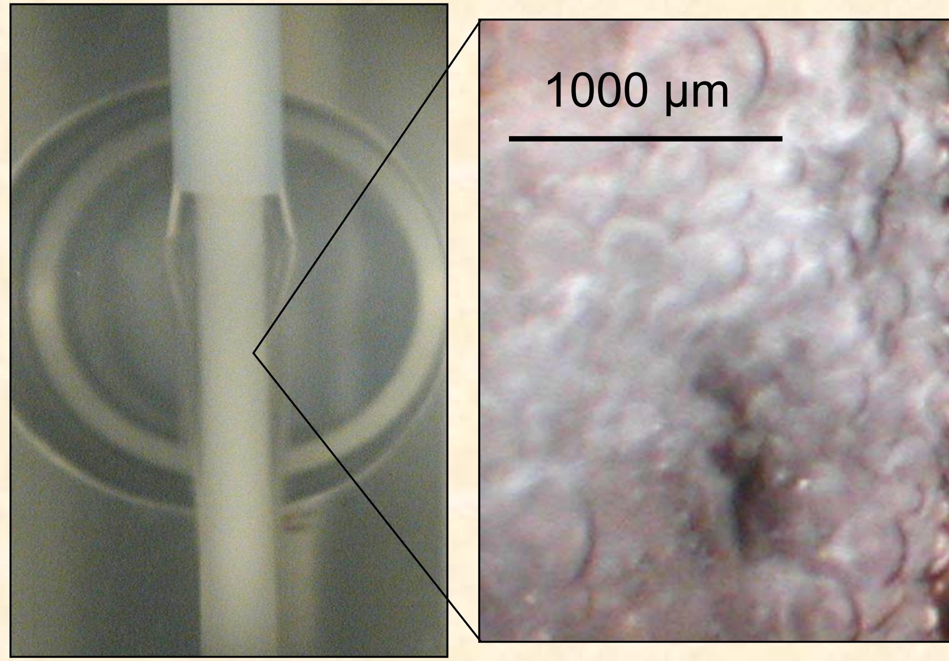
(72-L high pressure vessel)

ORNL SPS (Seafloor Process Simulator)

West et al., *AIChE J.*, 2003; Lee et al., *ES&T*, 2003

Laboratory Results Demonstrate the Sinking CO_2 Phase

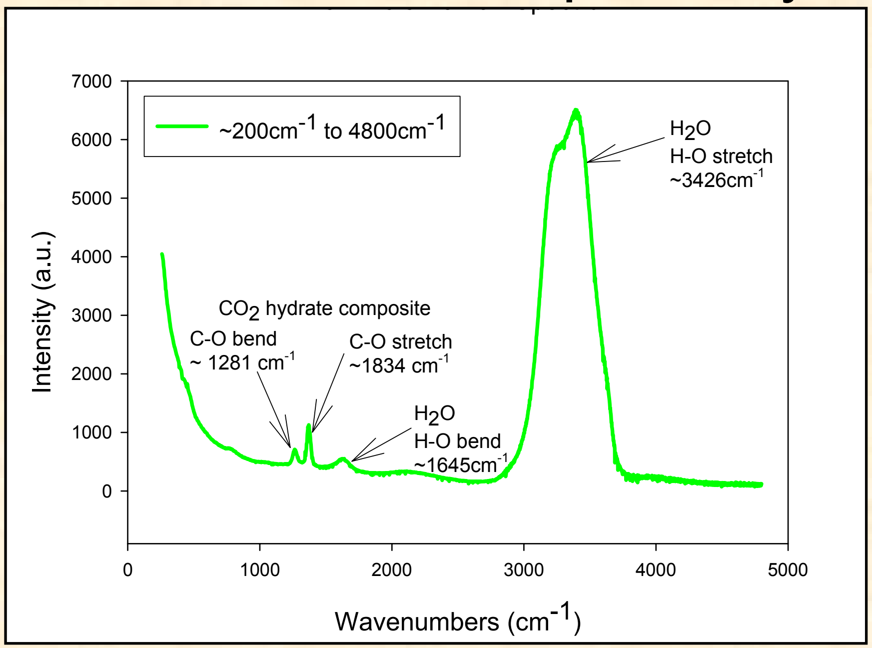




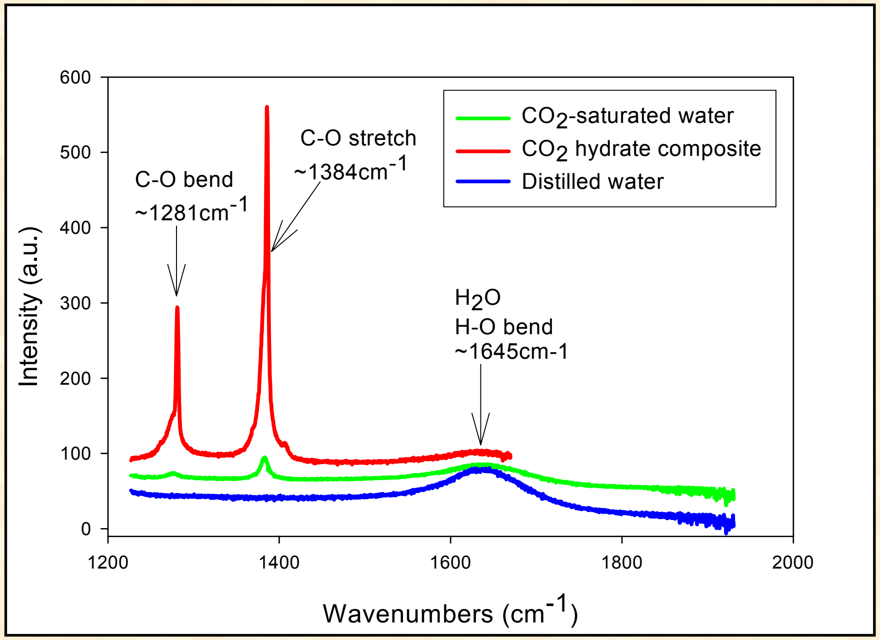
- Sinking CO_2 hydrate composite particles were demonstrated in the laboratory.
- Water injection capillaries used were 127 and 254 μm.
- The next step was characterization of composite, then field experiments to confirm results.

CO_2 Phases Identified in Composite

- The C-O Raman shifts demonstrate the presence of CO_2 hydrate in the composite.
- CO_2 hydrate has two peaks at ~1281 Δcm^{-1} and ~1384 Δcm^{-1} for the C-O bend and C-O stretch, respectively.
- Liquid CO_2 peaks are shifted up-field to ~1283 Δcm^{-1} and ~1387 Δcm^{-1}, respectively.

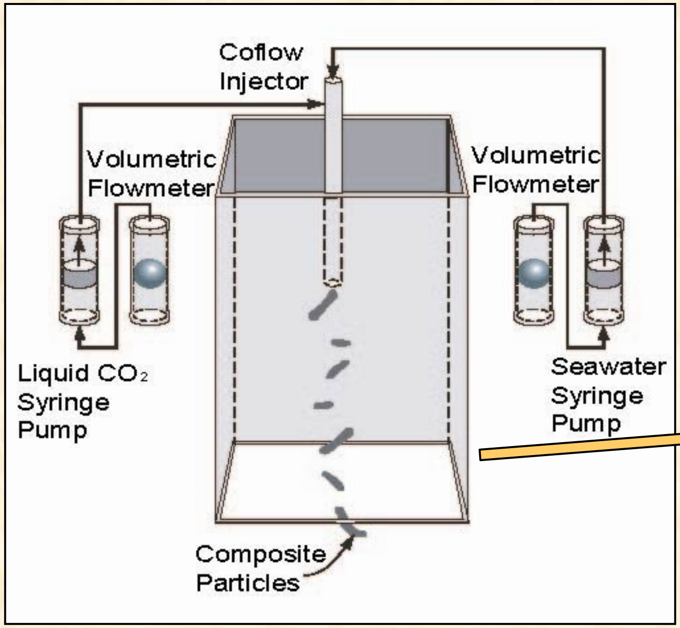


Wide range spectrum of CO_2 hydrate composite



Comparison of CO_2 spectra in hydrate and in water

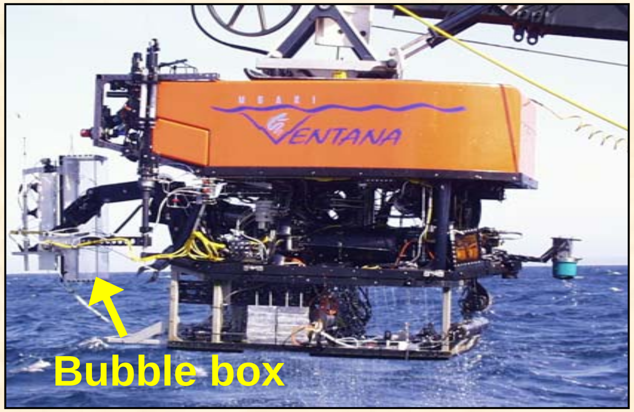
Ocean Injections in Monterey Bay, Ca



“Bubble box” for particle injection

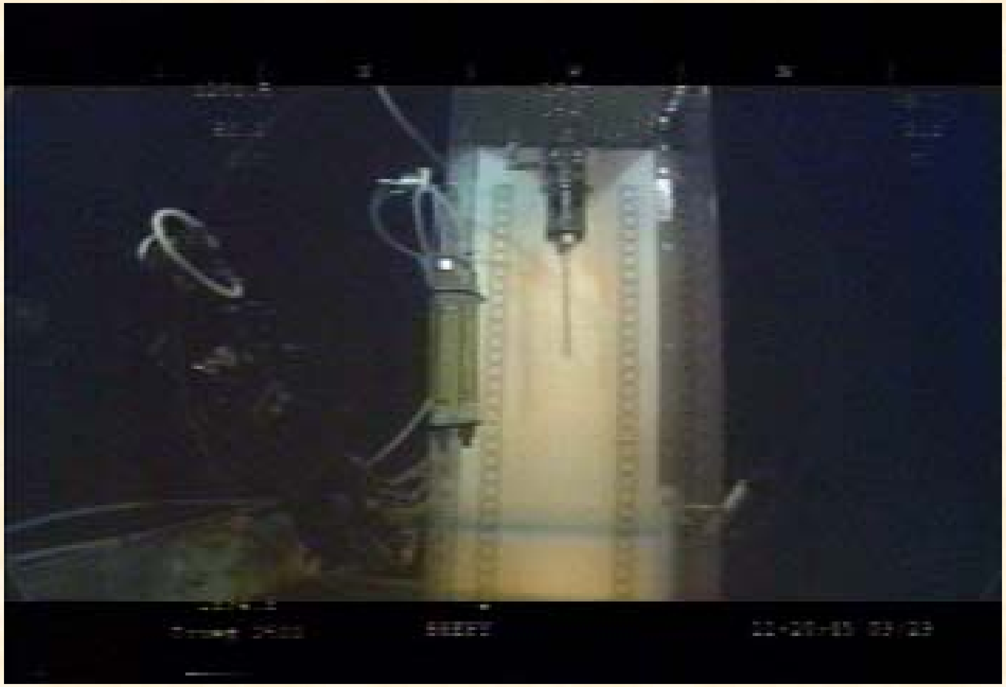
Plexiglass bubble box mounted on the ROV *Ventana*

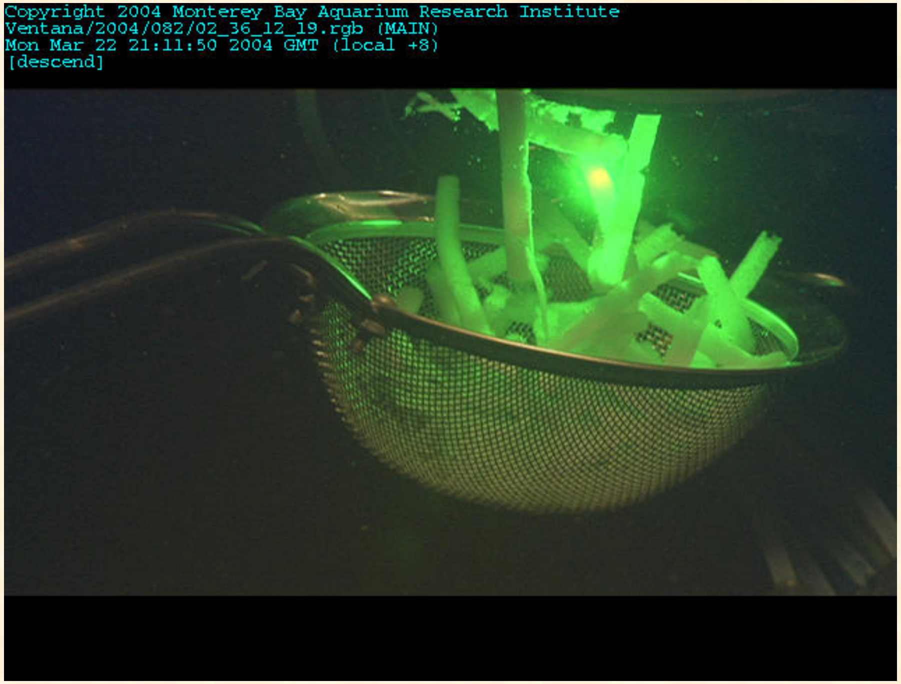
MBARI R/V Point Lobos



ROV Ventana

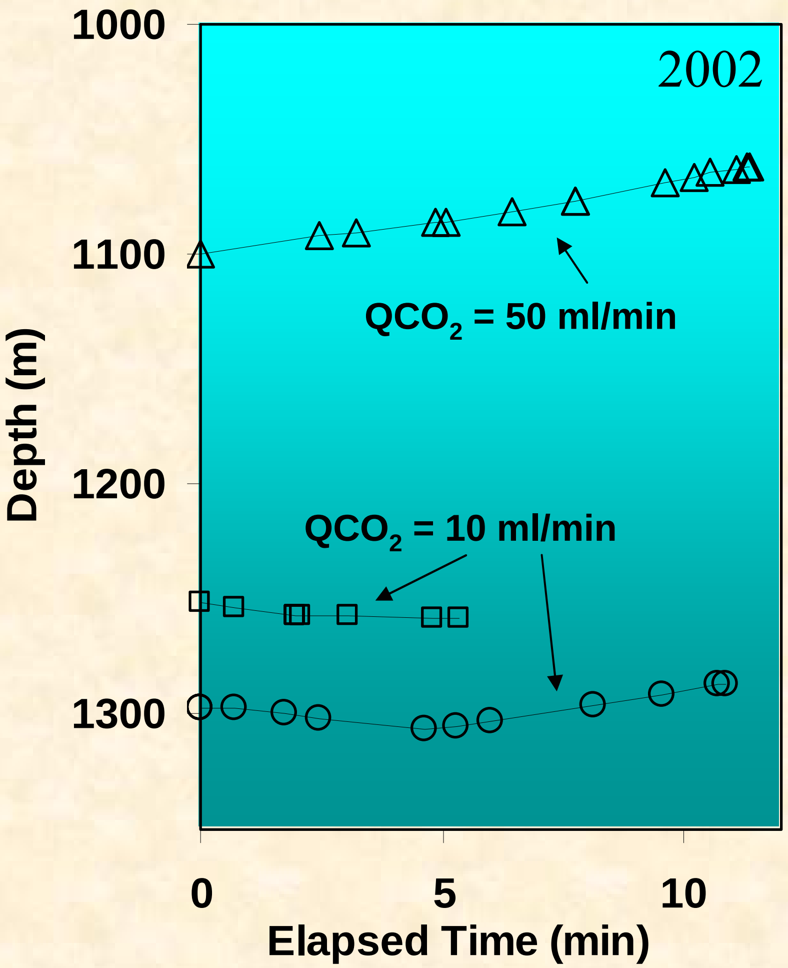
2004 Ocean Injection Results



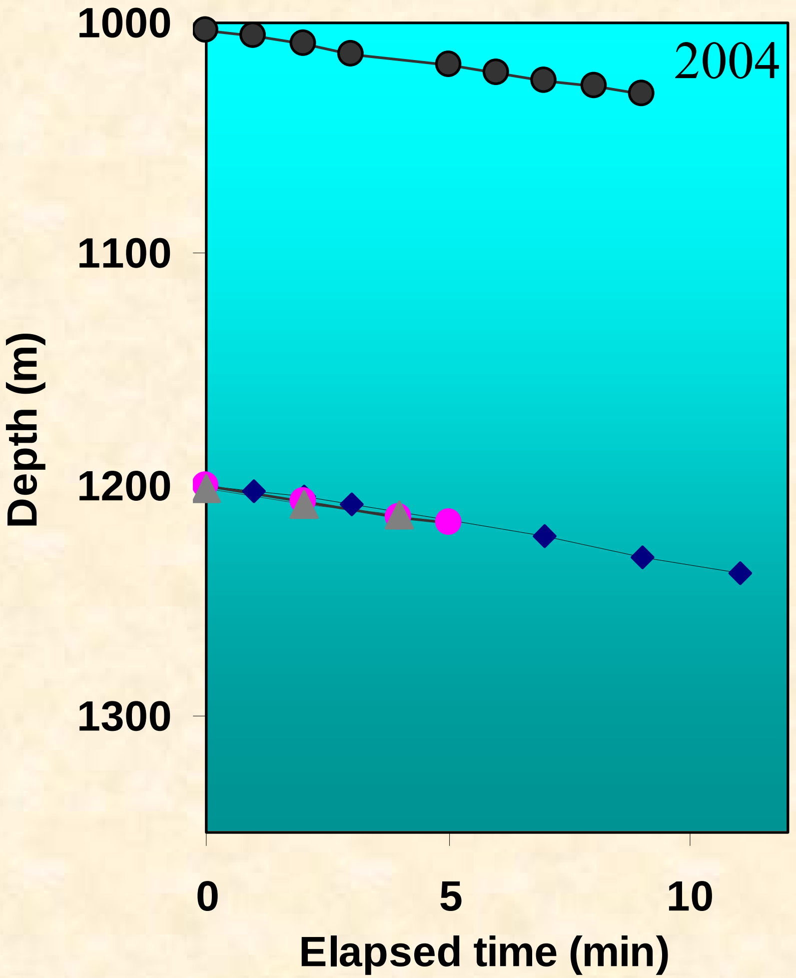


- A 381 μm capillary was used to inject water at 140 ml/min.
- CO_2 was injected at 26-36 ml/min.
- Hydrate composite particles were injected at 1000m and at 1200m.

2004 Particles Sank Consistently

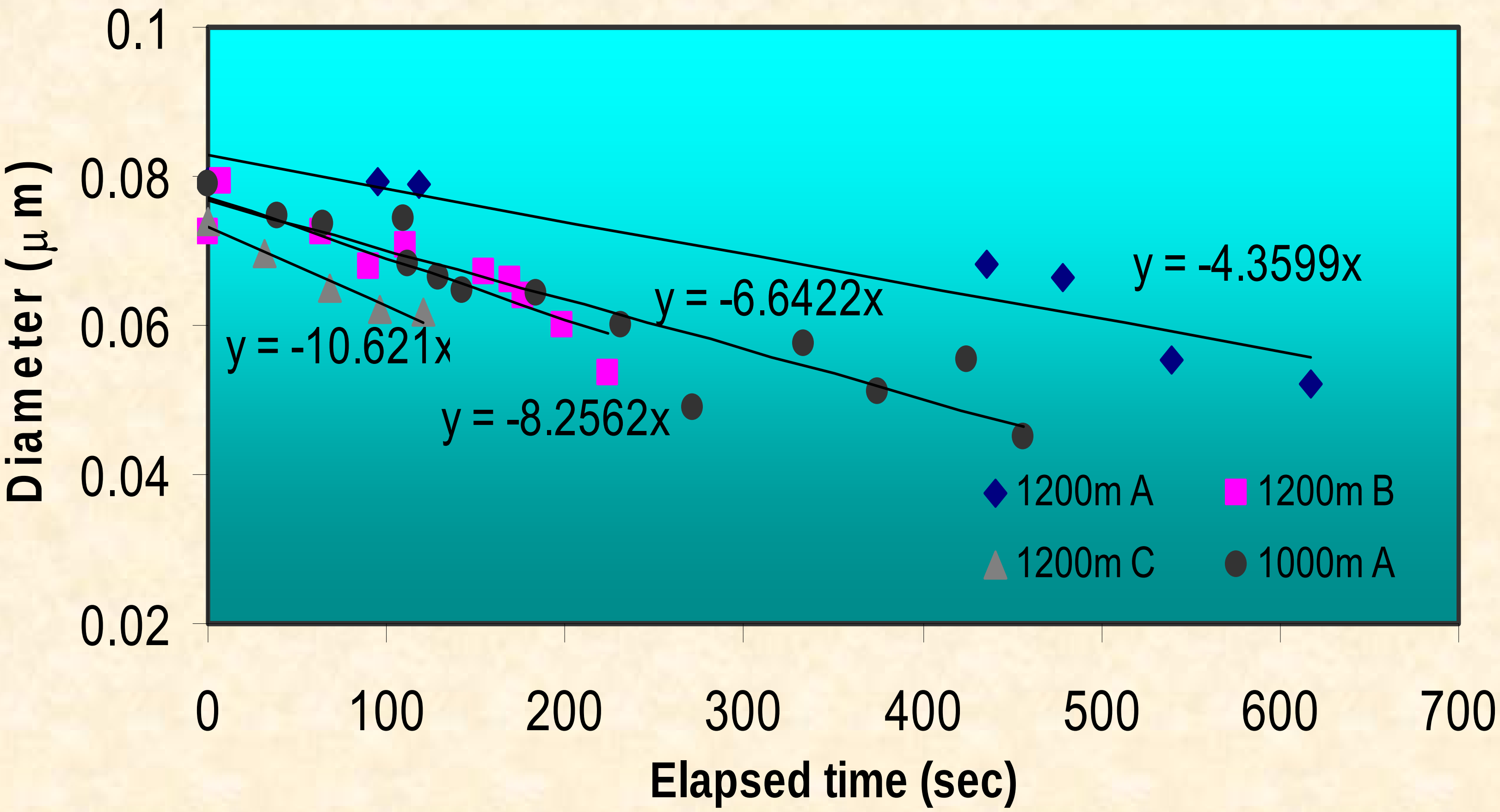


water capillary i.d. = 254 μm
outer tube i.d. = 6 mm
H_2O flow rate = 50 ml/min
CO_2 flow rates = 10-50 ml/min



water capillary i.d. = 381 μm
outer tube i.d. = 9 mm
H_2O flow rate = 140 ml/min
CO_2 flow rates = 26-36 ml/min

2004 Ocean Injection Results



- Composite particles shrank at 4.4-10.6 μm/s.
- Rehder et al. (2004) reported a pure CO_2 hydrate dissolution rate of 0.94-1.20 μm/sec at 1028m depth.

Rehder et al. *Geochim. Cosmochim. Acta* **2004**, *68*, 285-292.

Comparison of 2002 and 2004 Particles

	2004 Injections		2002 Injections		
depth (m)	1200 (A)	1000 (A)	1100	1250	1300
behavior	Sink	sink	float	sink	neutral
sinking rate (m/min)	3.5	3.1	-3.6 (float)	1.2	0
est. composite density (g/cm^3)	1.04(8)	1.04(6)	1.02(1)	1.04(5)	1.03(4)
est. composite conversion (x)	0.25	0.26	0.12	0.19	0.16
Composite shrink rt. ($\mu m/sec$)	4.4	6.6	5.3	7.4	4.1
CO_2 DR ($\mu mol/cm^2\ s$)	0.76	1.29	2.97	1.38	0.76

- 2004 particles appear to have more CO_2 converted to hydrate.
- Rehder et al. (2004) report pure CO_2 hydrate dissolution rate of 0.36 0.46 $\mu mol/cm^2 s$ and Brewer et al. (2002) report the dissolution rate of a rising CO_2 droplet as 3 $\mu mol/cm^2 s$.

Rehder et al. *Geochim. Cosmochim. Acta* **2004**, *68*, 285-292.
Brewer et al. *Environ. Sci. Technol.* **2002**, *36*, 5441-5446.

Uncertainty on Hydrate Conversion: Future Experiments

Variables	Values	Est. Hydrate Conversion
Particle Drag Coefficient	0.33	0.25
	1	0.46
	4	1.09
CO_2 Hydrate Density (g/cm^3)	1.143[a]	0.25
	1.12[b]	0.30
	1.10[c]	0.37
CO_2/H_2O in Particle	0.19	0.25
	0.46	0.21

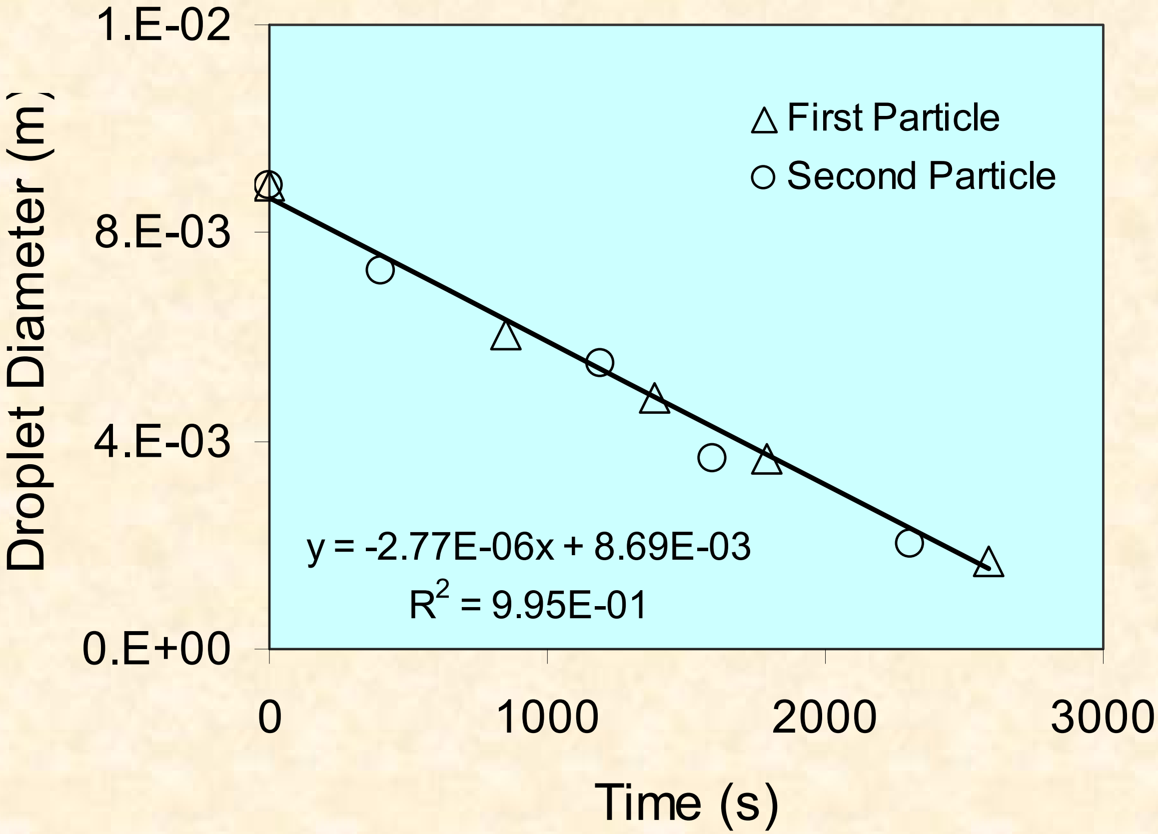
[a] Circone et al. *J. Phys. Chem. B*, 2003
[b] *Holder et al. Environ. Sci. Technol.* 1995
[c] Aya et al. *Energy* 1997

- Drag Coefficient:
  Particles may act more like rigid cylinders ≈ higher drag
- Hydrate Density:
  Precise value of CO_2 hydrate density still unknown
- CO_2/H_2O in particle:
  There may be significant water loss during injection

Dissolution Mechanism of Hydrate Covered CO_2 Droplets

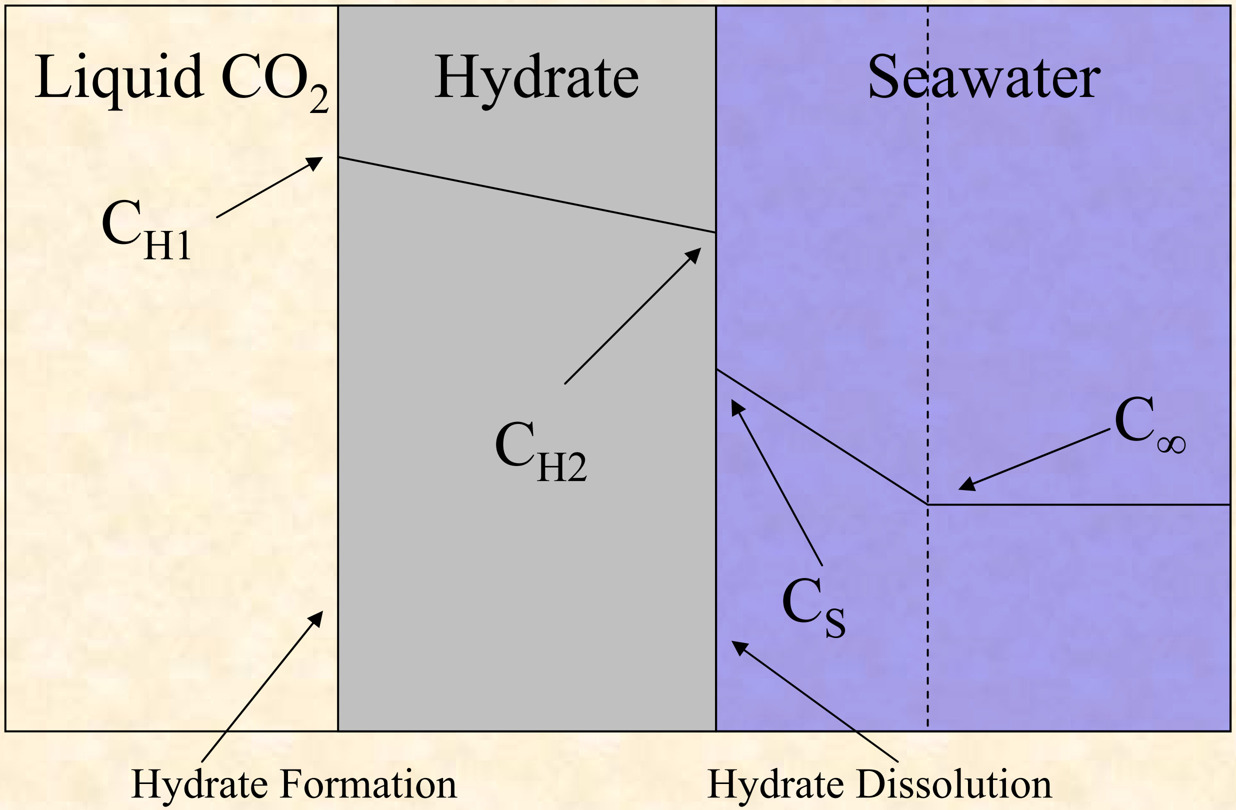
Modeling CO_2 dissolution in rising droplets of hydrate-covered CO_2 droplets released by Brewer et al. (ES&T, 2002).

Focus of study is on the controlling step in CO_2 dissolution.



Brewer et al. *Environ. Sci. Technol.* 2002

Heterogeneous Dissolution Model to Account for Multiple Phases*



C_{H1} = CO_2 conc. on liquid CO_2 side

C_{H2} = CO_2 conc. on H_2O side in the hydrate

C_s = CO_2 solubility in seawater

C_∞ = CO_2 conc. in seawater

- Hydrate layer may be impermeable (diffusion limited) or contain permeable capillaries*

*proposed by Mori and Mochizuki (Energy Conv. Manage., 1998)

Determination of the Limiting Step in Hydrate Dissolution

Overall dissolution ($\mathbf{k_T}$) is a function of hydrate layer mass transfer ($\mathbf{k_H}$) and CO_2 dissolution mass transfer ($\mathbf{k_D}$)*

$$J = \mathbf{k_T}\,(C_{H1} - C_{\infty})A_p$$

J = molar flow of CO_2
C_{H1} = CO_2 conc. on CO_2 side
C_{∞} = CO_2 conc. in seawater
A_p = reaction surface area

where $\mathbf{k_T} = s\, k_H\, k_D/(k_H + s\, k_D$

s = constant defined by $C_{H2} = s\, C_s$
C_{H2} = CO_2 conc. on H_20 side in the hydrate
C_s = CO_2 solubility in seawater

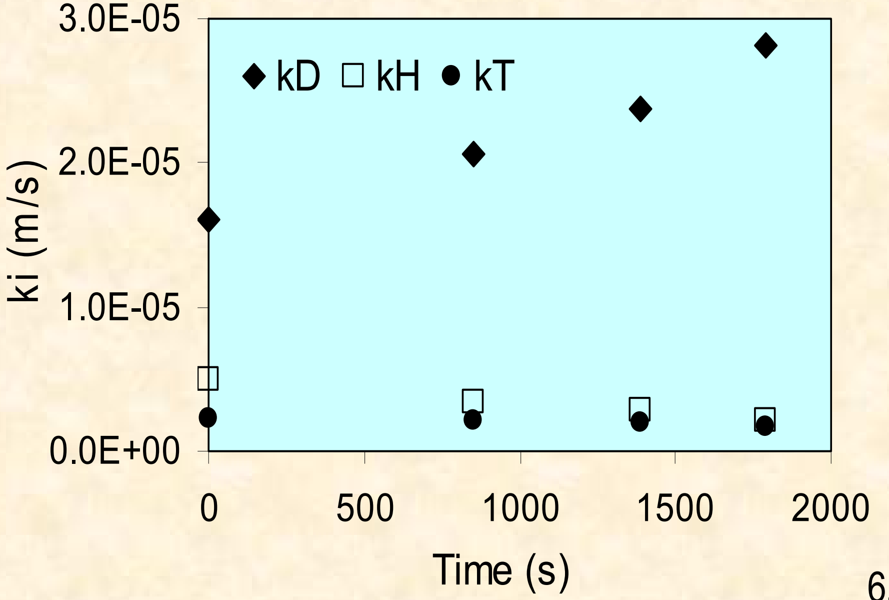
to determine $\mathbf{k_D}$: $Sh = 2 + 0.6\, Re^{0.5}\, Sc^{0.333}$ **

Sh = Sherwood Number = $\mathbf{k_D}\, d_p/D$, d_p= droplet diameter, D= CO_2 diffusivity
Re = Reynolds Number = $v\, d_p\, \rho/ \nu$, ν = seawater kinematic viscosity
Sc = Schmidt Number = ν/D

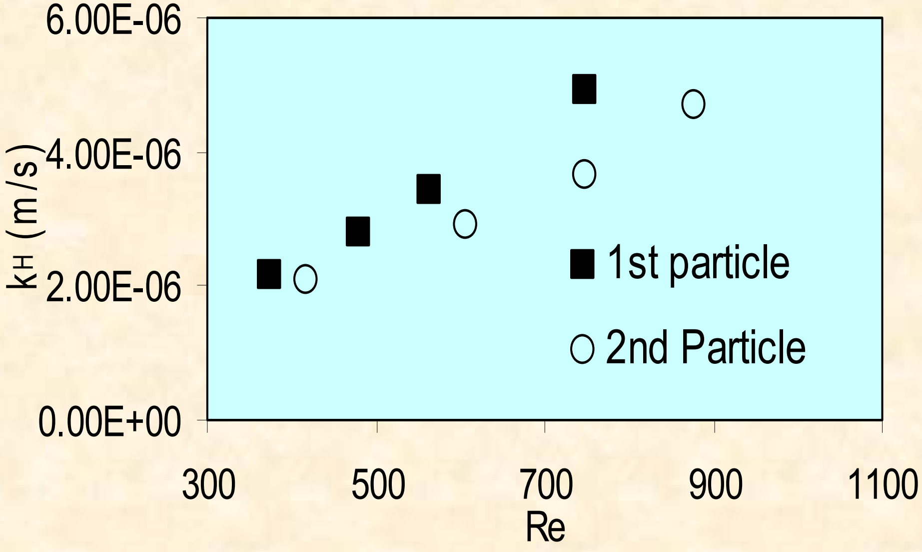
↳ use values for $\mathbf{k_T}$ and $\mathbf{k_D}$ to solve for $\mathbf{k_H}$

* from Ogasawara et al., (Energy and Fuels, 2001)   ** from Hirai et al. (Energy, 1997)

Mass Transfer through the Hydrate Layer is the Limiting Dissolution Step

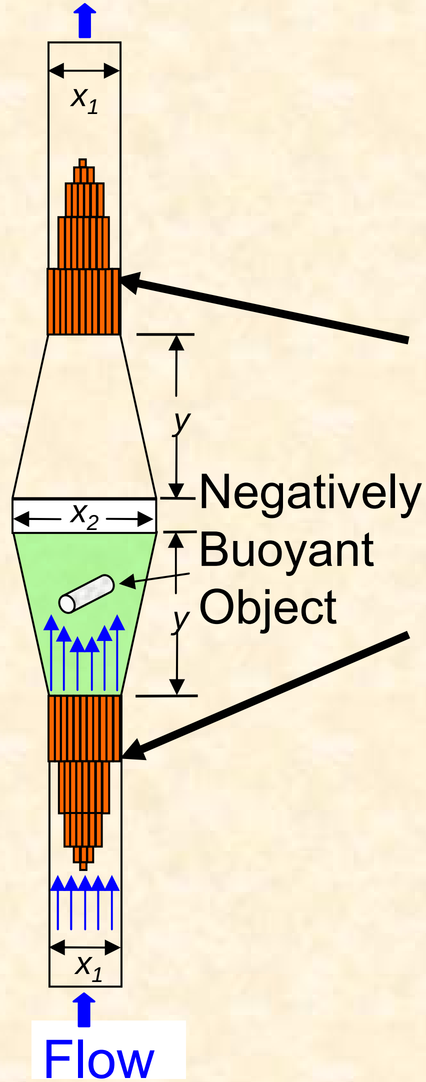


k_H appears to be the controlling step in mass transfer of CO_2



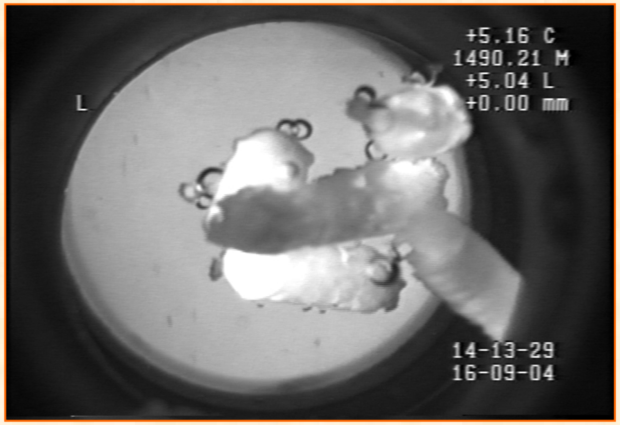
A positive relationship between k_H and the droplet Reynolds Number suggests the existence of capillaries in hydrate

Collaborative Work with Dr. Warzinski of NETL Using the High-Pressure Water Tunnel Facility

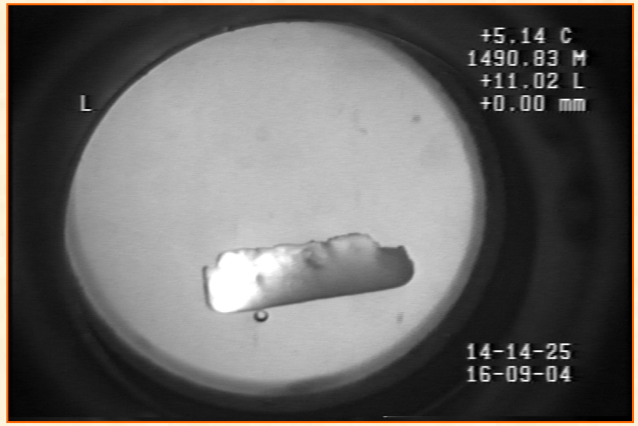


Flow Conditioning Elements

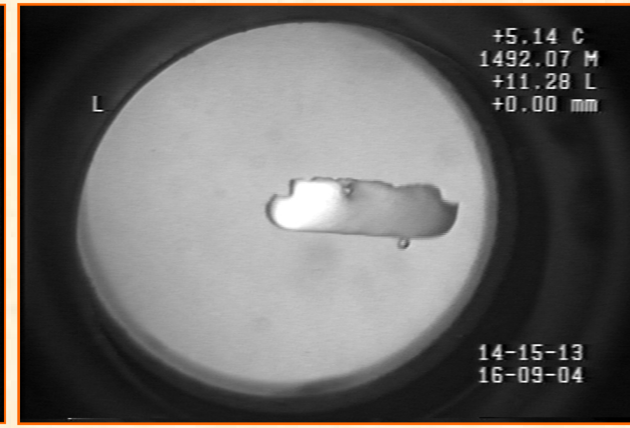
Particle Measurements in the HWTF



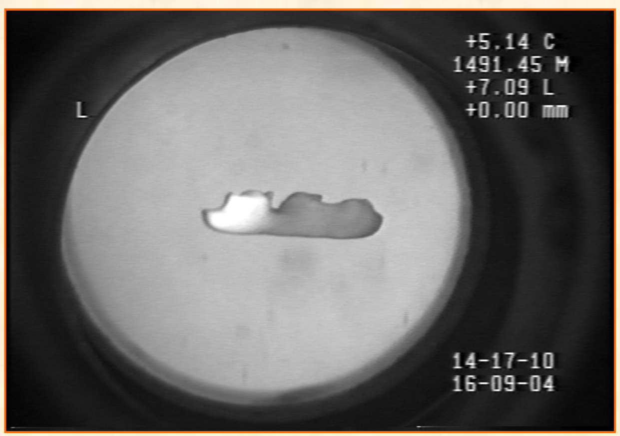
Elapsed Time = 103 s



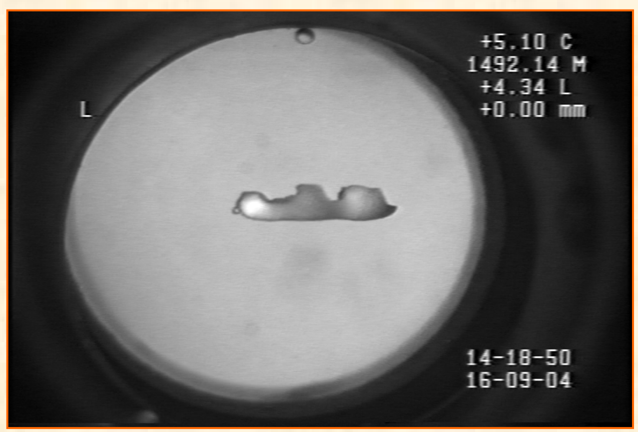
Elapsed Time = 157 s



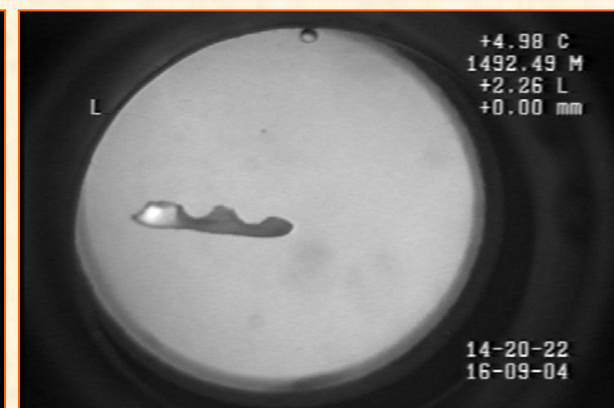
Elapsed Time = 205 s



Elapsed Time = 322 s



Elapsed Time = 422 s



Elapsed Time = 514 s

For more details on this work, see poster #85

Summary

- Ocean injections have demonstrated the formation of composite solid particles containing CO_2 hydrate, water, and liquid CO_2 at intermediate depths from the co-flow injection of ambient seawater and liquid CO_2
- Particles made by the larger injector in 2004 sank at a rate of 3 m/min which should carry CO_2 to deeper waters and lead to longer sequestration.
- Mass transfer modeling suggests that mass transfer through the hydrate layer is the controlling step in hydrate dissolution.

Acknowledgment

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