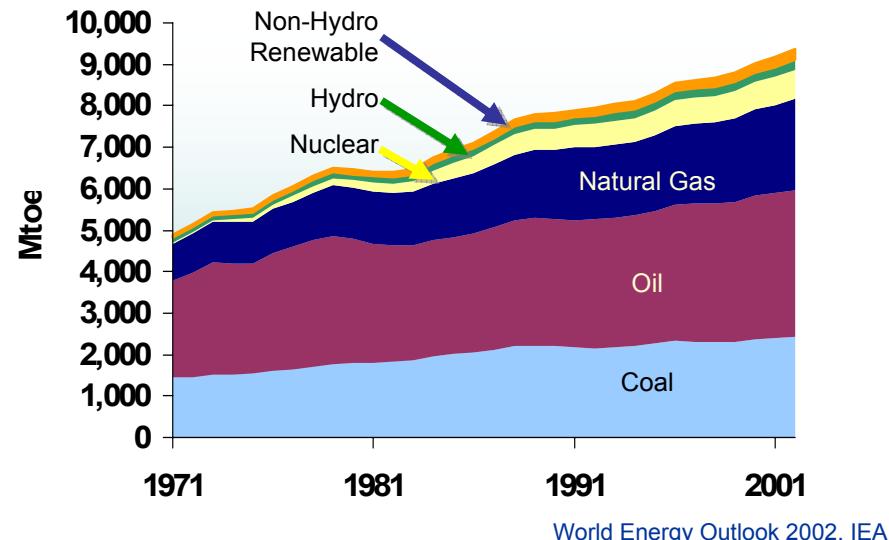


Role of Gas Hydrates in Energy Challenges

Costas Tsoiris
Oak Ridge National Laboratory
Georgia Institute of Technology

Energy challenges: energy security

World Primary Energy Demand



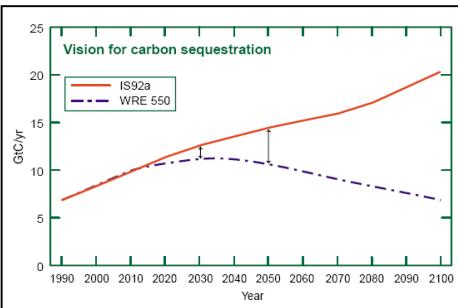
Energy challenges: environmental protection

Global Warming

- 7 Gt of carbon are released in the atmosphere every year
- CO₂ concentration in atmosphere increases
- Climate changes are currently observed



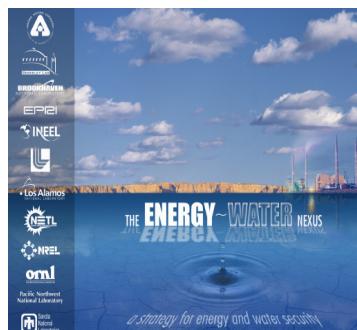
CEN, December 15, 2003



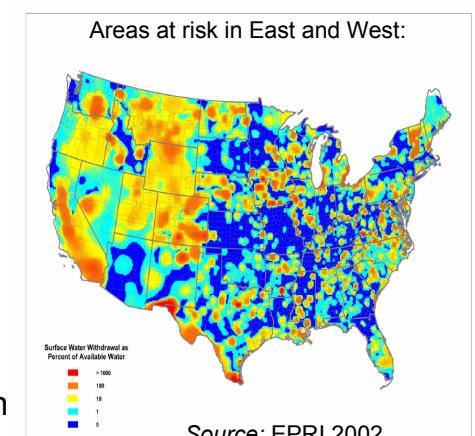
IS92a ⇒ "business as usual" or global warming
WRE 550 ⇒ atmospheric stabilization or reduction of CO₂ concentration to 550 ppm

175 GtC must be sequestered over a period of 50 years

Energy challenges: water availability



Each kilowatt-hour of electricity requires on average about 25 gallons of water to produce



Desired Future

- Energy security
- Environmental protection
- Social welfare
- Economic development

Complex problems - complex solutions

Reduce Carbon Intensity

- Renewables
- Nuclear

Improve Efficiency

- Demand Side
- Supply Side

Sequester Carbon

- Capture & Store
- Enhance Natural Processes

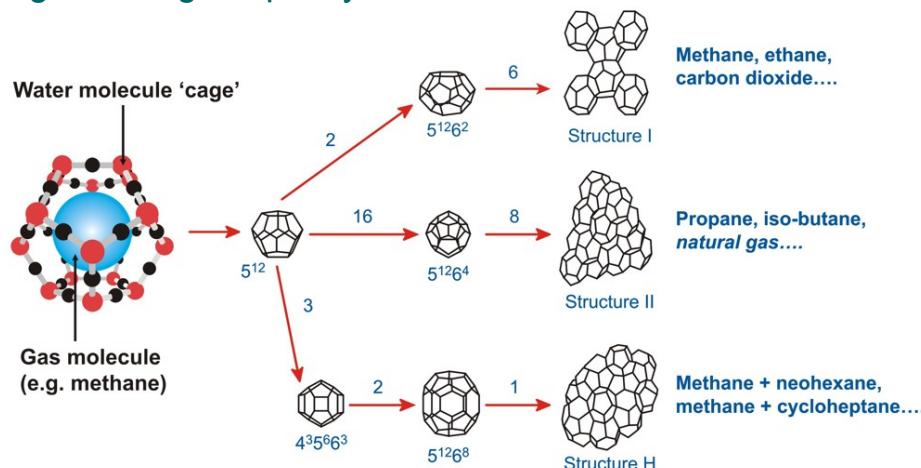
All options needed to:

- Supply energy demand
- Address environmental objectives



What are gas hydrates?

Crystalline, ice-like structures, stable at temperatures near 0 °C and pressures above 0.12 MPa, with large gas storage capacity

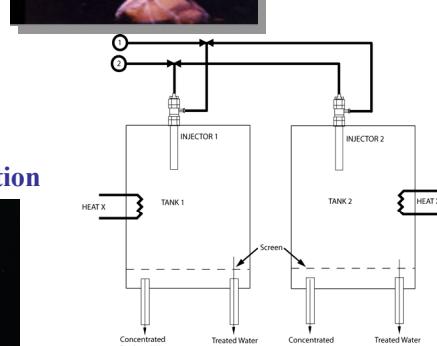


Gas hydrates can contribute to the solutions

Methane Hydrate Deposits



Methane hydrate on fire



CO₂ Hydrate for Carbon Sequestration



Water Desalination

Hydrate thermodynamic equilibrium

Multiphase equilibrium

$$\mu_w^H = \mu_w^I = \mu_w^{II} = \dots$$

$$\mu_1^H = \mu_1^I = \mu_1^{II} = \dots$$

$$\mu_2^H = \mu_2^I = \mu_2^{II} = \dots$$

Water in hydrate phase

If a standard state hydrate chemical potential is known at conditions (P,T), the only accountable change in energy is due to the occupation of hydrate cavities

$$\frac{\mu_w^H}{RT} = \frac{\mu_w^\beta}{RT} + \sum_m v_m \ln \left[1 - \sum_j \theta_{jm} \right]$$

(Parrish & Prausnitz, *IEC Proc. Des. Dev.*, 1972)

Cage occupancy

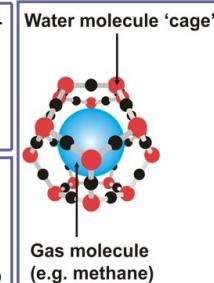
$$\theta_{jm} = \frac{C_{jm}}{1 + \sum_k C_{km} f_{km}}$$

(Van der Waals & Platteeuw, *Adv. Chem. Phys.*, 1959)

$$C_{jm} = \frac{4\pi}{kT} \int_0^{Rm-a_j} \exp \left[-\frac{\omega_{jm}(r)}{kT} \right] r^2 dr$$

Cell potential function of guest J in cage m: Kihara potential

(Ballard & Sloan, *Fluid Phase Equil.*, 2002)

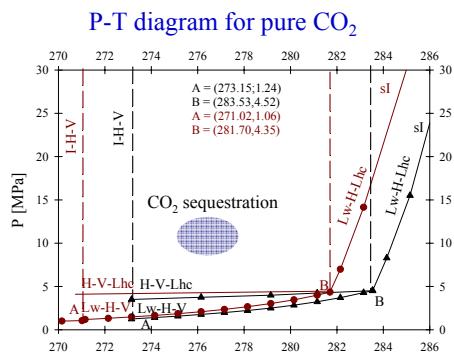


Empty hydrate cage

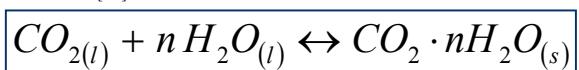
$$\frac{\mu_w^\beta}{RT_O} = \frac{\mu_w^O}{RT_O} - \int_{T_O}^T \frac{\Delta h_w}{RT^2} dT + \int_0^P \frac{\Delta v_w}{RT} dP - \ln a_w$$

(Parrish & Prausnitz, *IEC Proc. Des. Dev.*, 1972)

Salt affects CO₂ hydrate equilibria



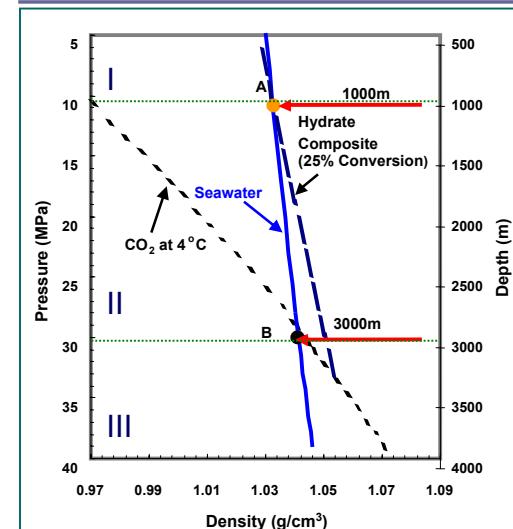
- Salt (3.5 w%) acts like an inhibitor, displacing hydrate stability zones to higher pressures and lower temperatures.
- Intermediate ocean depths are ideal for CO₂ hydrate formation.



Instantaneous, exothermic reaction limited by:

1. mass transfer barriers at the interface between reactants
2. dissipation rate of heat generated during reaction

CO₂ hydrate for ocean sequestration



- I. Rising plume of liquid CO₂ droplets
- II. Sinking plume of CO₂ hydrate
- III. Sinking plume of liquid CO₂ (lake in the bottom of the ocean)

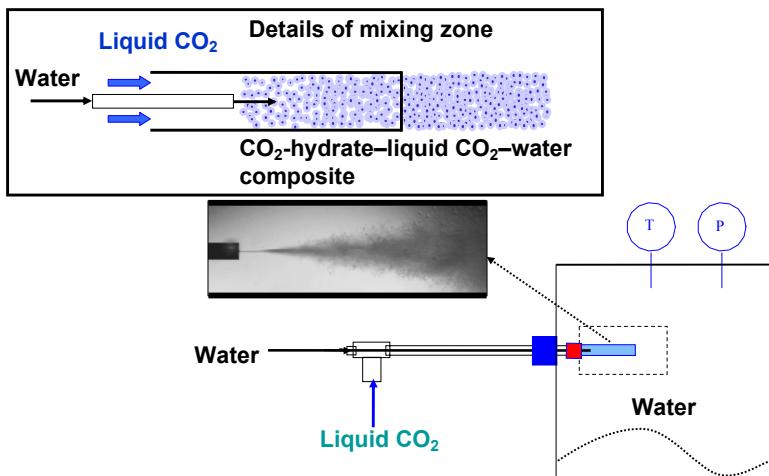
Factors to consider:

1. Environmental impacts
2. Residence time of carbon in the ocean
3. Operational costs

CO₂-ocean sequestration purposes \Rightarrow minimum conversion dictated by injection depth and temperature (typically 0.25)

A three-phase reactor for CO₂ hydrate formation

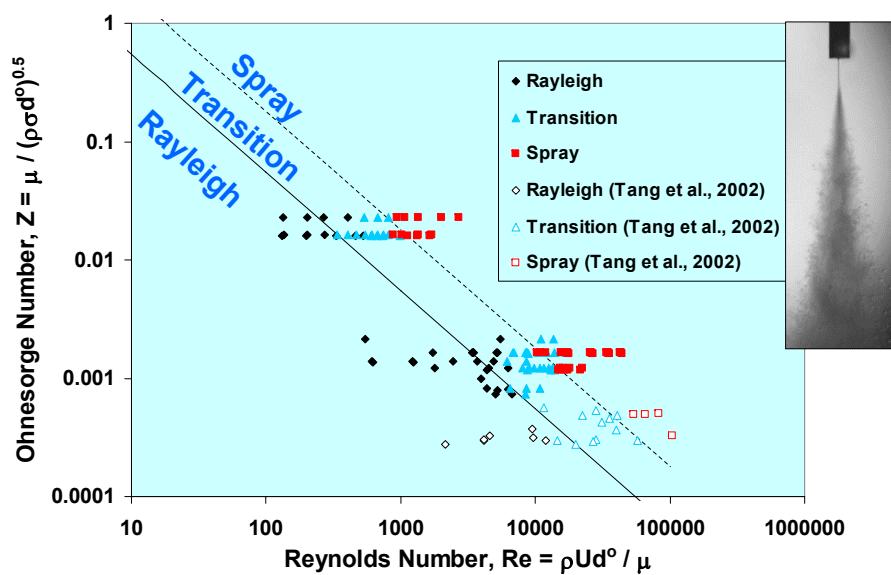
- The continuous-jet hydrate reactor (CJHR) rapidly mixes two fluids to create a solid composite



U.S. Patent # 6,598,407 (2003)

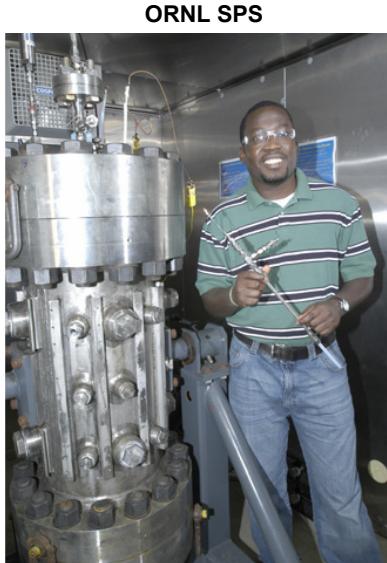
West et al., AIChE J. (2003); Lee et al., ES&T (2003)

Jet breakup regimes



Riestenberg et al., American Mineralogist (2004)

The CJHR with the ORNL seafloor process simulator



Floating and sinking hydrate composite

Liquid CO₂ injections alone produced CO₂ droplets lighter than ambient water at test pressure (4 °C, 10 MPa)



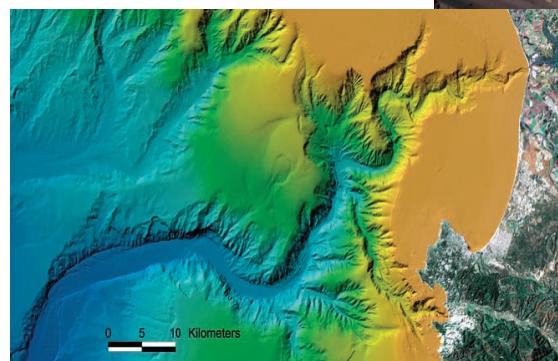
The CO₂/water flowrate ratio determines the density of the composite

Experiment in Monterey Bay using Point Lobos

Western Flyer with ROV Tiburon



Point Lobos with ROV Ventana

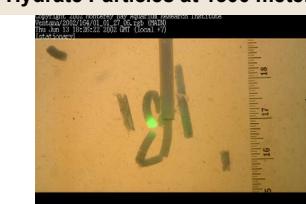


First ocean CO₂ experiment (2002)

From Oak Ridge National Laboratory



Injection of Neutrally Buoyant CO₂ Hydrate Particles at 1300 meters



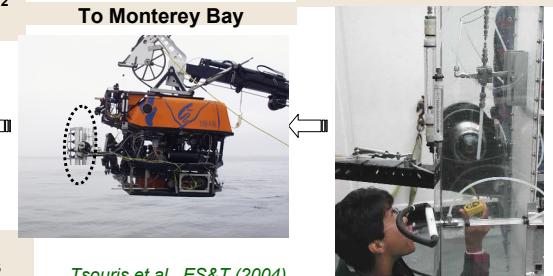
Raman spectrometer used for analysis of CO₂ hydrate particles

To Monterey Bay Aquarium Research Institute



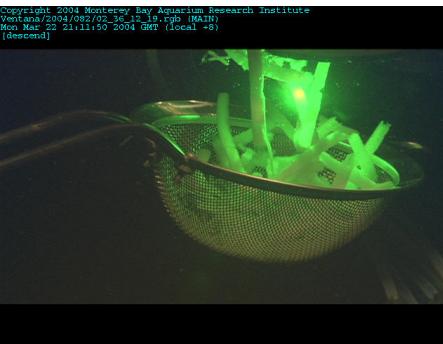
(Installation of injector with Raman spectrometer)

To Monterey Bay



Tsouris et al., ES&T (2004)

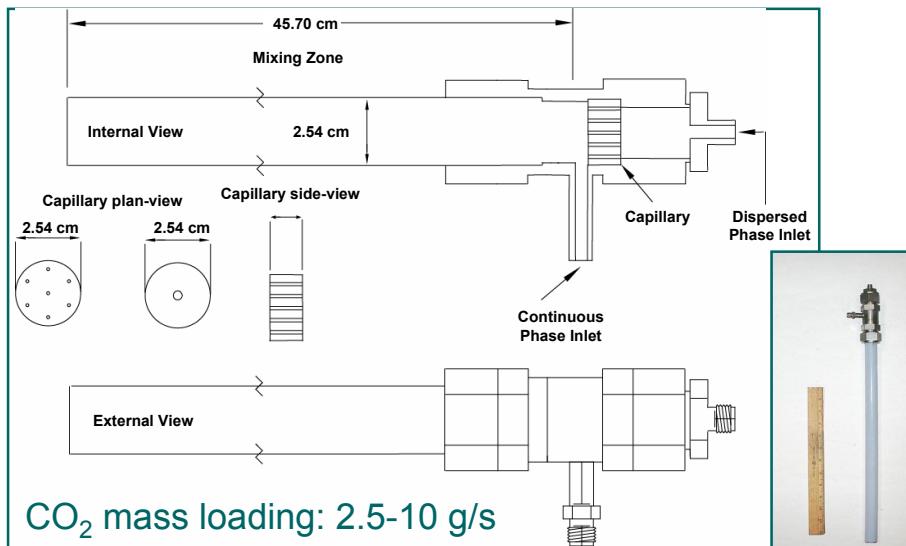
Raman experiment in the deep ocean (2004)



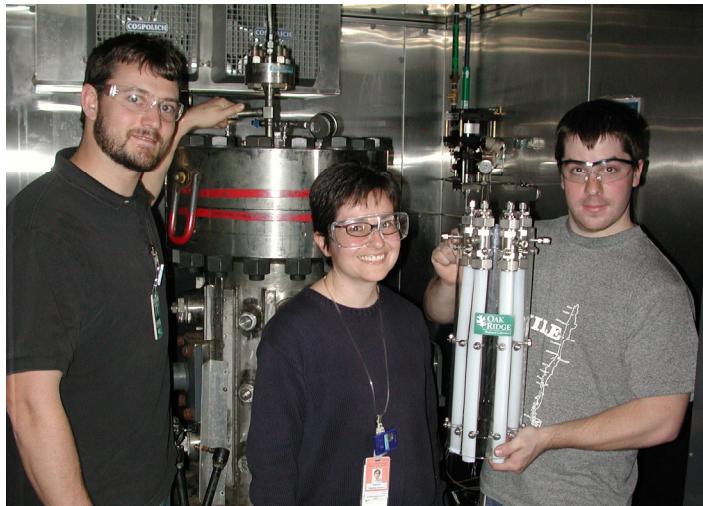
- Successfully performed Raman spectroscopy in the deep ocean
- Carried out studies at 1,000-1,500 m using a larger injector
- Formed composite particles sinking at a speed of 3-4 m/min
- Estimated the conversion of liquid CO₂ to hydrate to be 35-40%

Riestenberg *et al.*, ES&T (2005)

The scale-up geometry of the CJHR



Scale-up of the continuous-jet hydrate reactor



Goal:

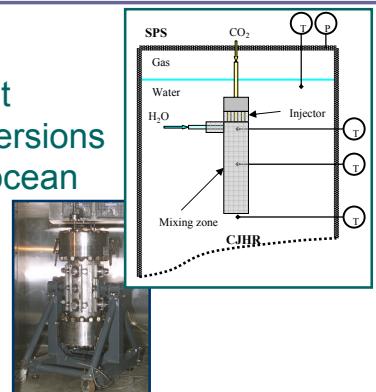
- Increase flow-rates by two orders of magnitude

Scale-up Rules:

- Spray regime
- Good mixing
- Single/multiple capillaries
- Constant residence time
- Constant flow-rate ratio

Testing the CJHR

Determination of the operation conditions and injector design that allows the CJHR to achieve conversions greater than 0.2 at conditions of ocean intermediate depths



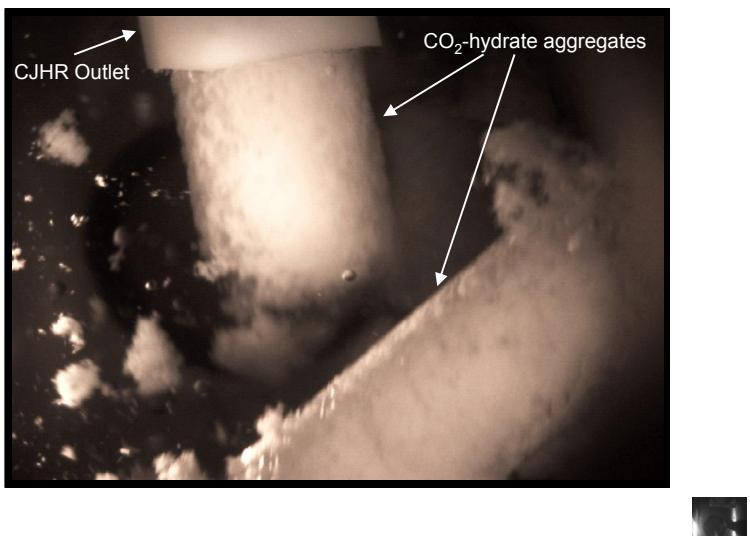
Laboratory-scale:

CO₂ mass load = 0.2 – 0.8 g/s
Conversion = 0.15 – 0.20
Operation pressure = 13.0 MPa
Temperature = 2 – 6 °C
Diameter = 0.5 cm

Pilot-scale:

CO₂ mass load: up to 10 g/s
Conversion: > 0.20
Operation pressure: <13.0 MPa
Temperature = 2 – 6 °C
Diameter: 2.54 cm

The CJHR in operation



CO_2 vs. H_2O as dispersed phase

CO ₂ dispersed			
Injector	D [mm]	T [°C]	P [MPa]
Single	3.175	4.0	—
Single	2.381	5.0	7.6
Multiple	1.191	5.1	6.9
Multiple	0.397	4.2	6.2

H ₂ O dispersed			
Injector	D [mm]	T [°C]	P [MPa]
Single	3.969	4.5	—
Single	3.175	4.5	—
Multiple	1.588	4.0	—
Multiple	1.191	2.5	13.1

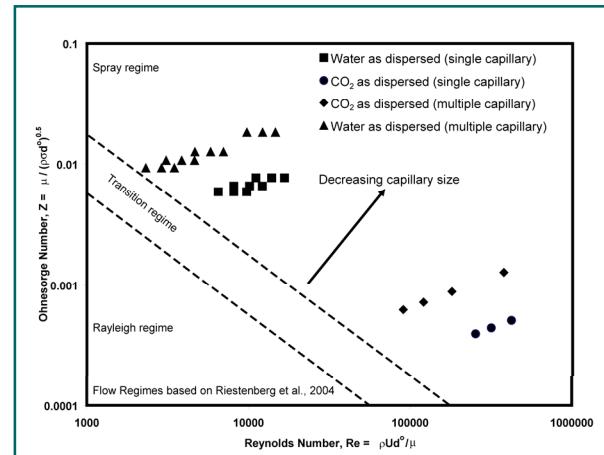
CO_2 as dispersed phase \Rightarrow **consolidated, sinking hydrate** at pressures as low as 6.2 MPa (~ 850 m) and typical intermediate depth ocean temperatures

Multiple-capillary injectors \Rightarrow lower operation pressures



$X > 0.2 \Rightarrow$ effective control over mass-transfer barriers

Hydrodynamics inside the CJHR



1. Single-capillary injectors with internal diameter [mm]: 3.969, 3.175, 2.381, 1.588, 1.191, 0.794, 0.397

2. Multiple-capillary injectors with internal diameter [mm]: 1.588, 1.191, 0.794, 0.397

All injectors tested \Rightarrow mixing conditions in spray regime

Distilled water vs. seawater

Distilled water				Seawater			
P [MPa]	H ₂ O:CO ₂	T [°C]	Hydrate	P [MPa]	H ₂ O:CO ₂	T [°C]	Hydrate
11.7	3.0	4.4	C,S	13.1	4.5	1.9	C,S
7.6	3.0	4.1	C,S	11.7	4.5	1.6	C,S
6.7	3.0	4.1	C,S	11.7	3.0	1.5	C,S/NB
6.2	3.0	4.2	U,NB	11.7	3.0	3.0	C,NB

C = consolidated, U = unconsolidated, S = sinking, NB = neutrally buoyant

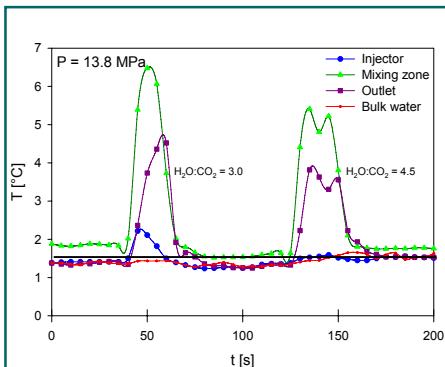
Seawater:

- \Rightarrow decrease in activity of water due to dissolved salt
- \Rightarrow displacement of hydrate equilibrium towards **lower T and higher P**



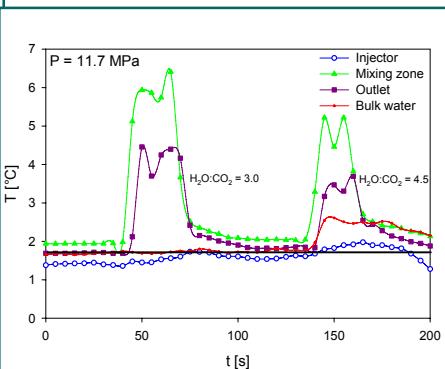
Lower conversions in seawater \Rightarrow thermal effects?

Thermal effects

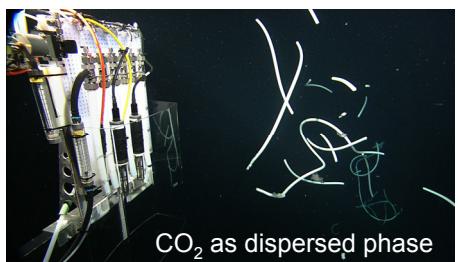


Higher $\text{H}_2\text{O}:\text{CO}_2$ ratios \Rightarrow more effective heat removal from the reaction plane and higher conversions

Local high T \Rightarrow local unfavorable thermodynamic conditions for hydrate formation

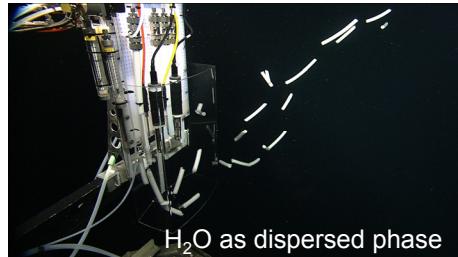


Sequestering CO_2 with the CJHRs



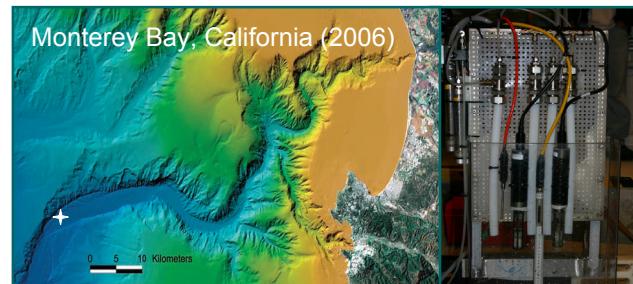
CO_2 as dispersed phase

Production of **consolidated, sinking hydrate particles** at intermediate ocean depths (1200 – 2000 m)

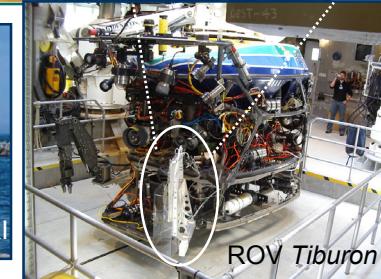


- H_2O as dispersed phase more effective in the field
- Plume of slowly dissolving particles (average life time 18 min)
- Maximum pH increase at injection point = 0.15

The scaled-up CJHR in the field

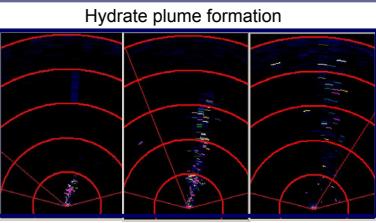
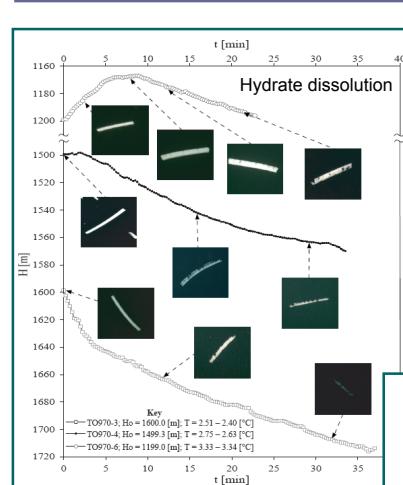


Battery of four CJHR in series
 CO_2 load = 30 g/s
Depth = 1200 – 2000 m



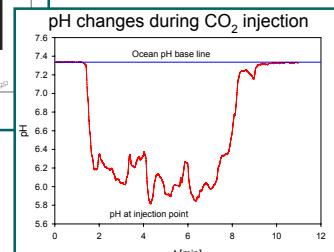
ROV Tiburon

Valuable information obtained from the field



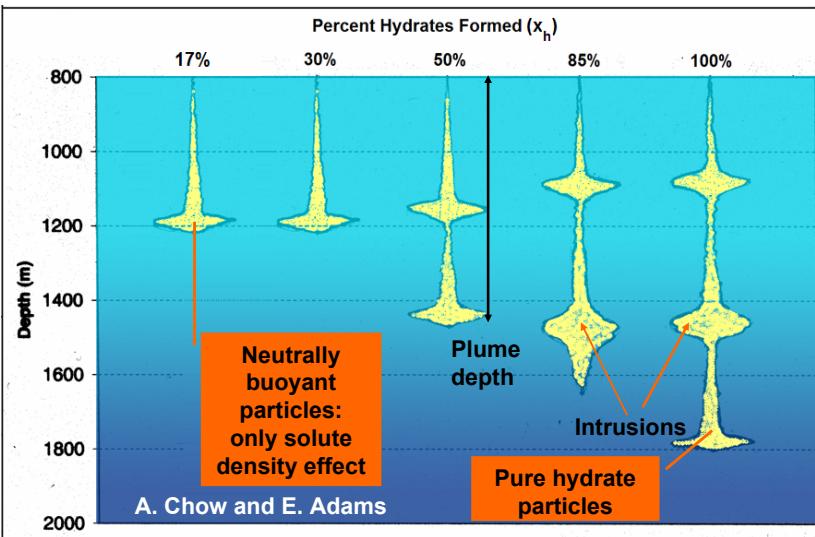
Sonars:
1500 m
8 m/div

Hydrate plume formation
Plume modeling \Rightarrow assessment of feasibility and impact of large-scale injection operations

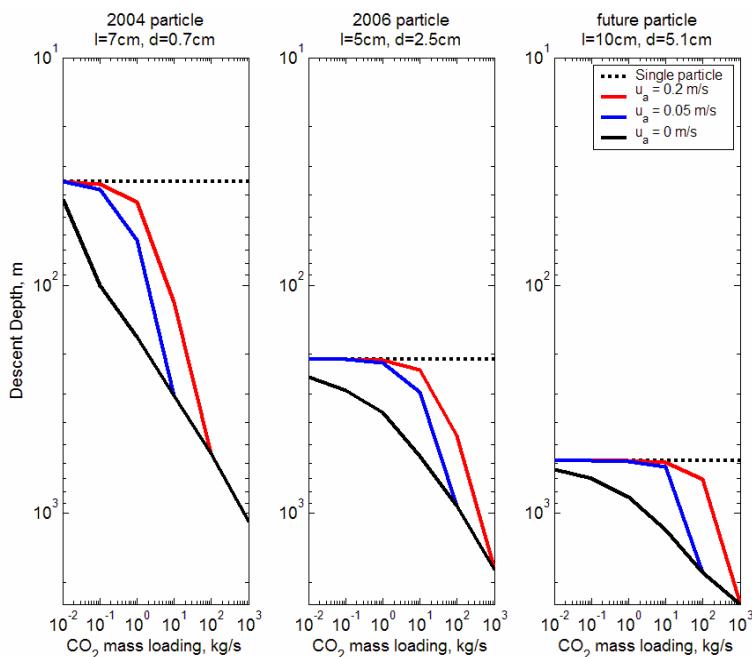


Hydrate particle behavior in ocean: plume modeling

(100 kg/s CO₂, 1 cm diameter spheres, release depth 800 m, Q_c/Q_w = λ = 0.49)

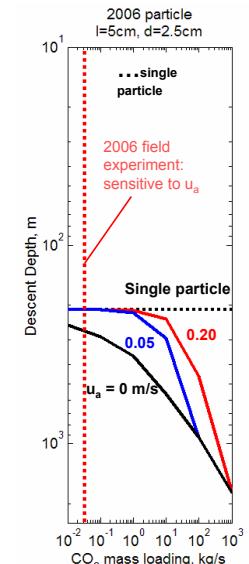


Collaborative work conducted by Eric Adams at MIT



Effect of cross flow and mass loading

- Larger mass loading
 - Deeper sinking
 - Weaker cross flow effect
- Smaller mass loading
 - Stronger cross flow effect
- Stronger current
 - Stronger cross flow effect
- Increasing particle diameter
 - Deeper sinking
 - Stronger cross flow effect



Carbon sequestration approaches

Separation and Storage



Deep Ocean
Injection



Unmineable
Coal Seams

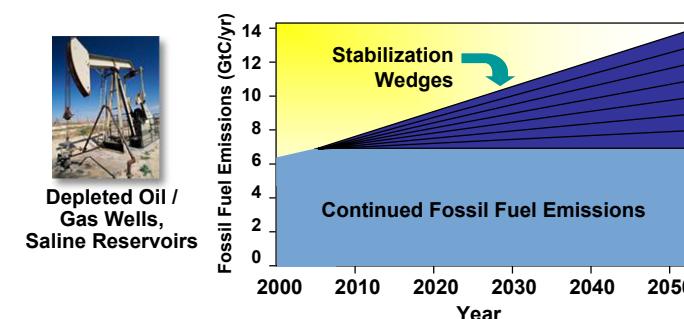
Enhance Natural Processes



Enhanced
Photosynthesis

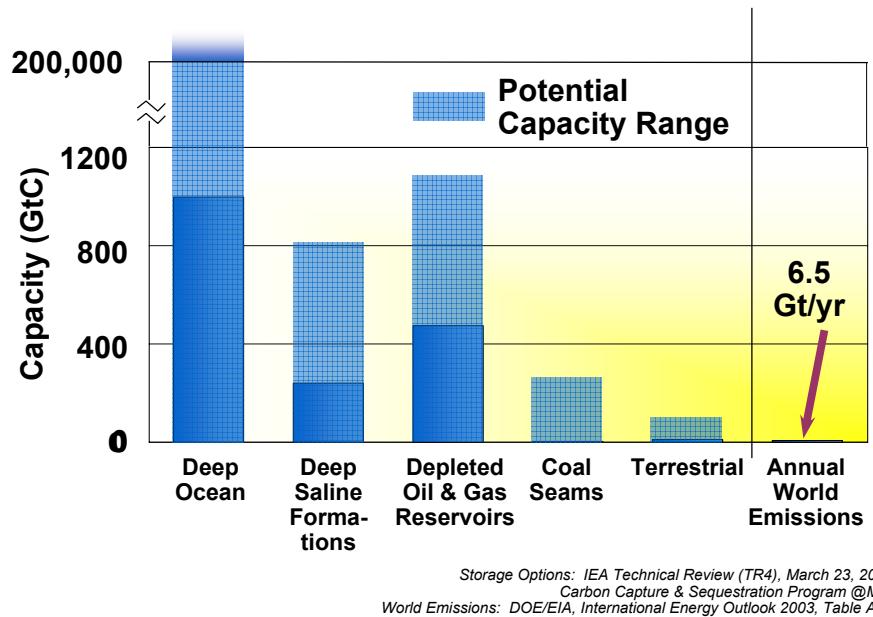


Forestation



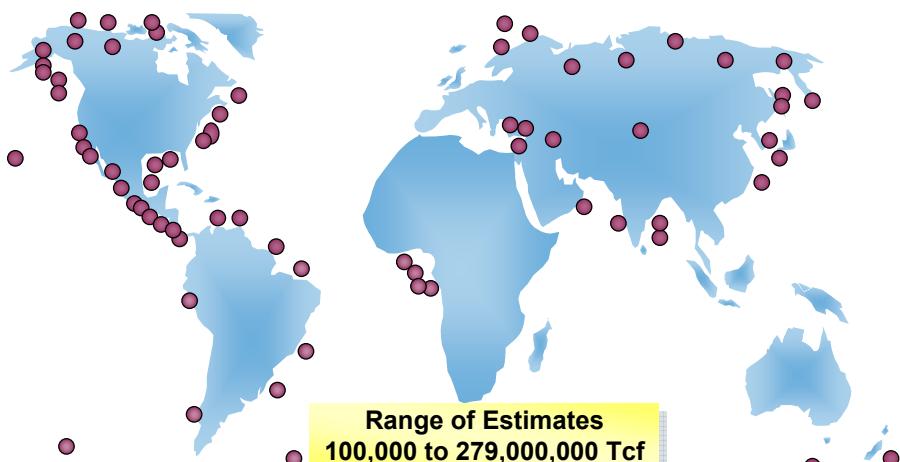
Iron or Nitrogen
Fertilization of
Ocean

Large potential storage capacity for the deep ocean



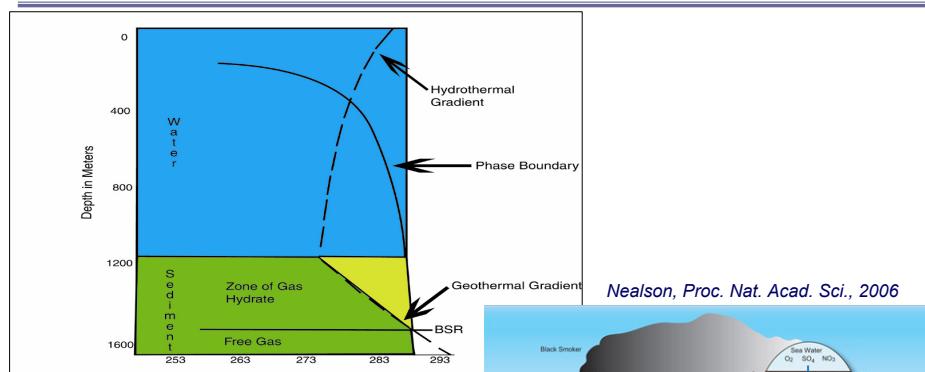
Natural gas hydrates: future energy source

Methane Hydrate Deposits



Adapted from U.S. Geological Survey, based on K.A. Kvenvolden, "Methane Hydrate – A Major Reservoir of Carbon in the Shallow Geosphere?" Chemical Geology, Vol. 71 (1988)

Why gas hydrate form in sediments?

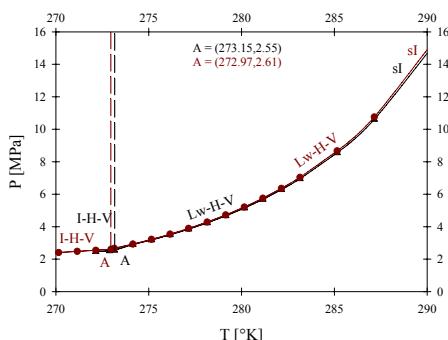


- Low temperature
- High pressure
- High gas concentration

<http://news.nationalgeographic.com/news/bigphotos/86824375.html>

CH₄ hydrate equilibria: effect of salt (0.3 w%)

P-T diagram for pure CH₄



Current focus

- Hydrate dissociation kinetics
- Effects of pressure, temperature, external forces, shear stress

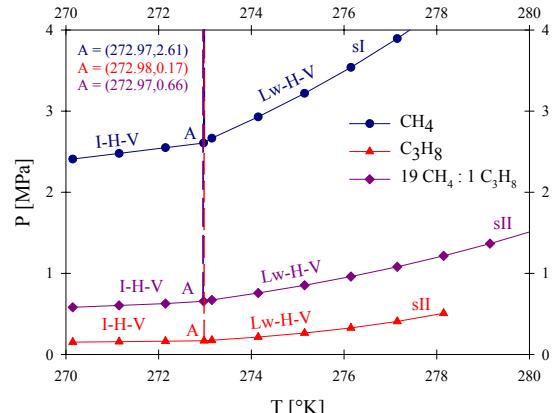
Challenges

- Hydrate is widely spread
- Sediment stability

Other applications of methane hydrates

- Natural gas transportation (safer than LNG)
- Gas separation

Mixed hydrates: produced water desalination



- Gas hydrates can be used for coalbed-methane produced water desalination. Salt is excluded from the hydrate structure.
- Methane requires high pressures for hydrate formation
- Small quantities of propane may decrease the pressure significantly.

Other applications of gas hydrates

Natural gas transportation (safer than LNG)
Hydrogen storage (with THF)
Gas separation

Acknowledgments

- Office of Biological and Environmental Research
- Office of Fossil Energy, U.S. DOE
- Monterey Bay Aquarium Research Institute



Field Experiment, Monterey Bay (April, 2006)