A Continuous-Jet Hydrate Reactor for Ocean Carbon Sequestration:

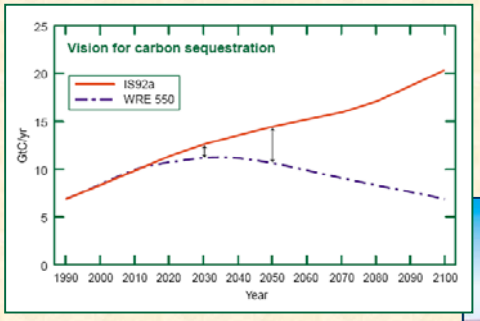
Laboratory and Field Experiments

C. Tsouris, P. Szymcek, P. Taboada-Serrano, S.D. McCallum
Oak Ridge National Laboratory

P.G. Brewer, E.T. Peltzer, P. Walz
Monterey Bay Aquarium Research Institute

A.C. Chow, E.E. Adams
Massachusetts Institute of Technology

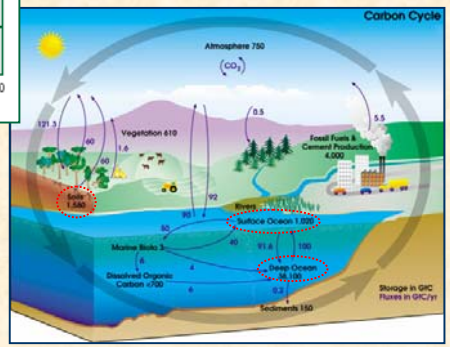
Greenhouse gases – the challenge



From "Carbon Sequestration Research and Development", DOE Report, 1999.

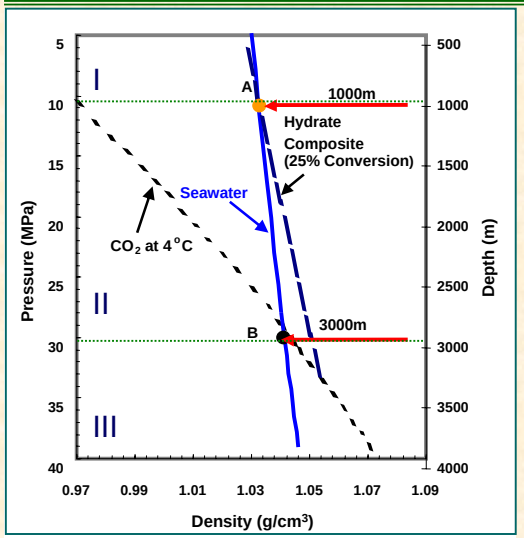
IS92a ⇒ "business as usual" or global warming

WRE 550 ⇒ atmospheric stabilization or reduction of CO_2 concentration to 550 ppm



175 GtC must be sequestered over a period of 50 years

Ocean carbon sequestration



I. Rising plume of liquid CO_2 droplets

II. Sinking plume of CO_2 hydrate

III. Sinking plume of liquid CO_2 (lake in the bottom of the ocean)

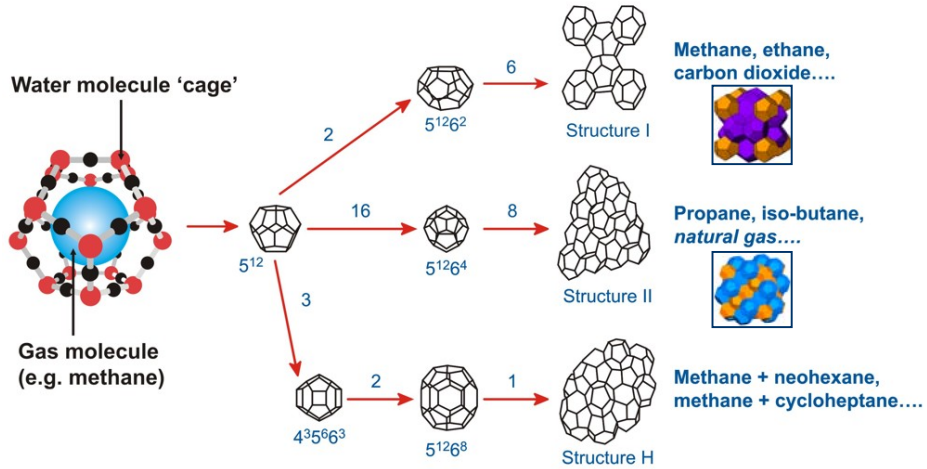
Factors to consider:

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

For CO_2-ocean sequestration purposes: minimum required conversion is dictated by injection depth and temperature (typically 0.20-0.25)

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



Hydrate thermodynamic equilibrium

Multiphase equilibrium

$$\mu_w^H = \mu_w^I = \mu_w^{II} = \ldots$$
$$\mu_1^H = \mu_1^I = \mu_1^{II} = \ldots$$
$$\mu_2^H = \mu_2^I = \mu_2^{II} = \ldots$$

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"

$$\frac{\mu_w^H}{RT} = \frac{\mu_w^\beta}{RT} + \sum_m \upsilon_m \ln\left[1 - \sum_J \theta_{Jm}\right]$$

(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)

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

(Statistical Mechanics)

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

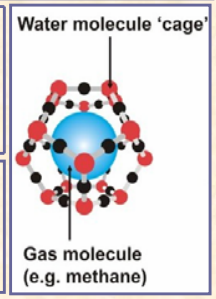
(Ballard & Sloan, *Fluid Phase Equil.* 2002)

Empty hydrate cage

(Classical Thermodynamics)

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

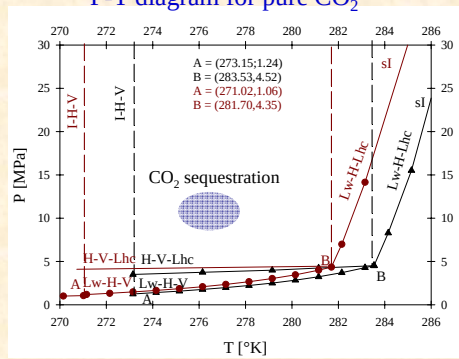
(Parrish & Prausnitz, *IEC Proc. Des. Dev.*, 1972)



(CGHR – Heriot Watt University, U.K.)

Salt affects CO_2 hydrate equilibria

P-T diagram for pure CO_2



- Salt (3.5 w%) acts like an inhibitor, displacing hydrate stability zones to higher pressures and lower temperatures.
- Intermediate ocean depths are ideal for CO_2 hydrate formation.
- Ocean CO_2 sequestration in the form of hydrate is possible.

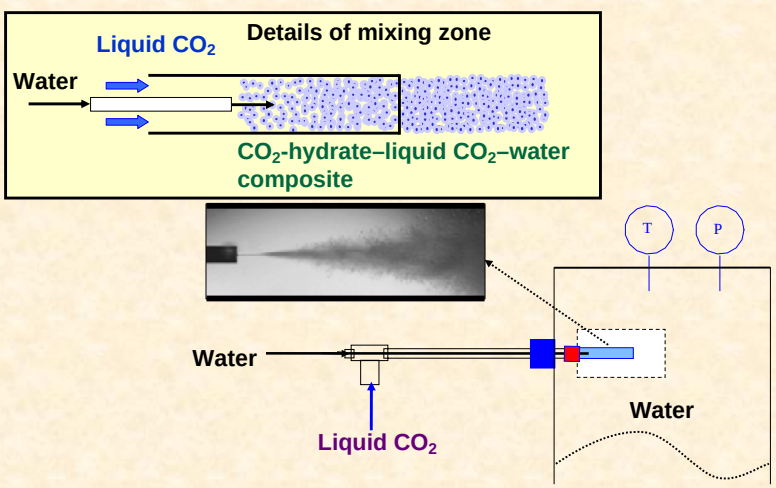
$$CO_{2(l)} + n\,H_2O_{(l)} \leftrightarrow CO_2 \cdot nH_2O_{(s)}$$ (Physical reaction)

Instantaneous, exothermic reaction limited by:

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

A three-phase reactor for CO_2 hydrate formation

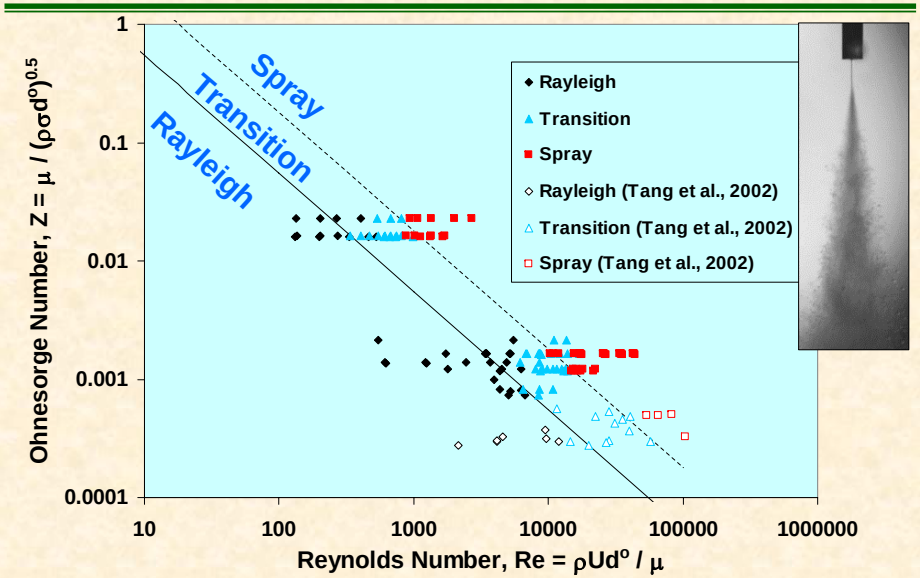
- The continuous-jet hydrate reactor (CJHR) rapidly mixes two fluids to create a solid composite



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

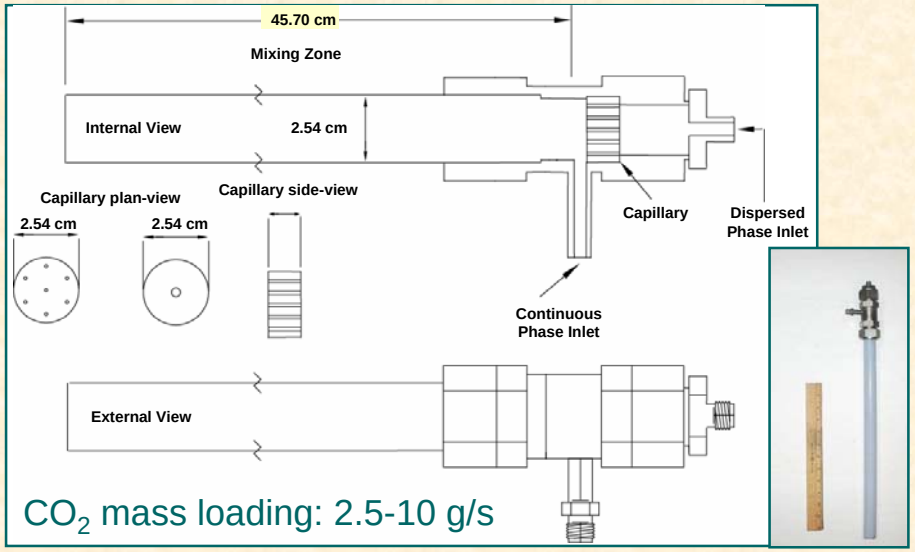
West et al., AIChE J. (2003); Lee et al., Env. Sci. &Technol. (2003)

Jet breakup regimes



Riestenberg et al., American Mineralogist (2004)

The continuous-jet hydrate reactor (CJHR)

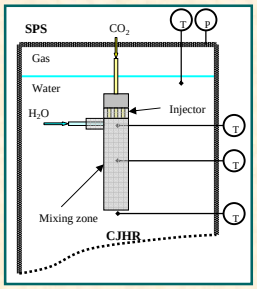


CO_2 mass loading: 2.5-10 g/s

Testing the CJHR

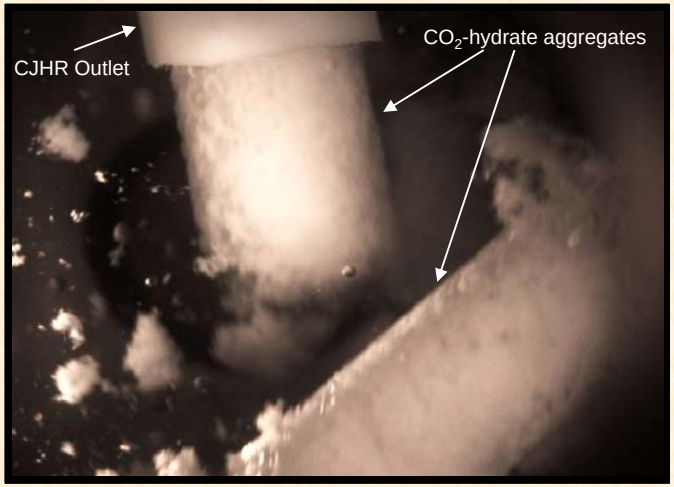
Determination of the operation conditions and injector design that allows the CJHR to achieve conversions greater than 0.2 at conditions of ocean intermediate depths

- Seafloor process simulator (SPS), a hastelloy vessel of 72 L
- Pressure and temperature monitoring
- Visualization

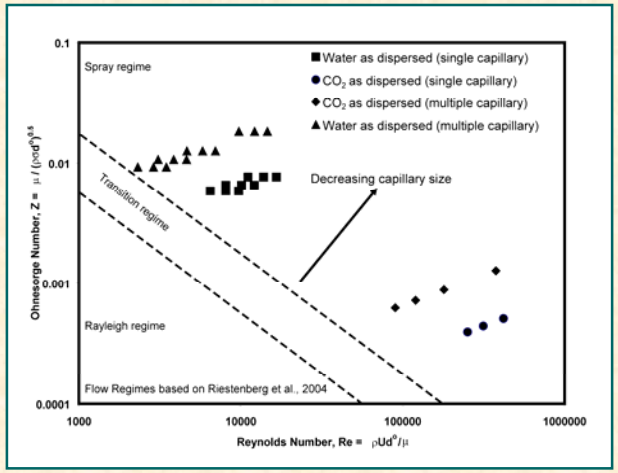


ORNL SPS

The CJHR in operation



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 ⇒ mixing conditions in spray regime

CO2 vs. H2O 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_2O 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 ⇒ **consolidated, sinking hydrate** at pressures as low as 6.2 MPa (~ 610 m) and typical intermediate depth ocean temperatures

Multiple-capillary injectors ⇒ lower operation pressures

X > 0.2 ⇒ effective control over mass-transfer barriers

Distilled water vs. seawater

Distilled water

P [MPa]	$H_2O:CO_2$	T [°C]	Hydrate
11.7	3.0	4.4	C,S
7.6	3.0	4.1	C,S
6.7	3.0	4.1	C,S
6.2	3.0	4.2	U,NB

Seawater

P [MPa]	$H_2O:CO_2$	T [°C]	Hydrate
13.1	4.5	1.9	C,S
11.7	4.5	1.6	C,S
11.7	3.0	1.5	C,S/NB
11.7	3.0	3.0	C,NB

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

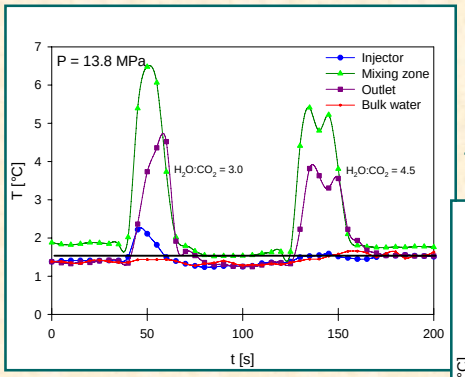
Seawater:

⇒ decrease in activity of water due to dissolved salt

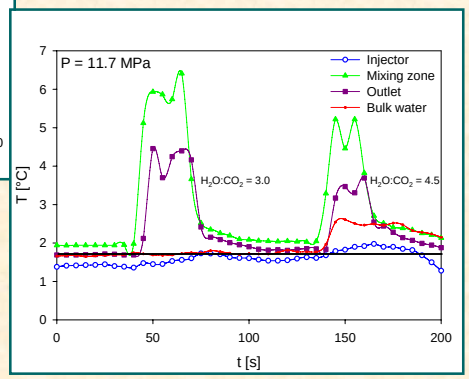
⇒ displacement of hydrate equilibrium towards lower T and higher P

Lower conversions in seawater ⇒ thermal effects?

Thermal effects

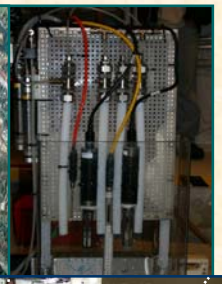


Local high T ⇒ local unfavorable thermodynamic conditions for hydrate formation



Higher $H_2O:CO_2$ ratios ⇒ more effective heat removal from the reaction plane and higher conversions

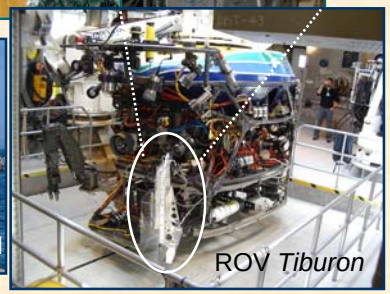
The CJHR in the field



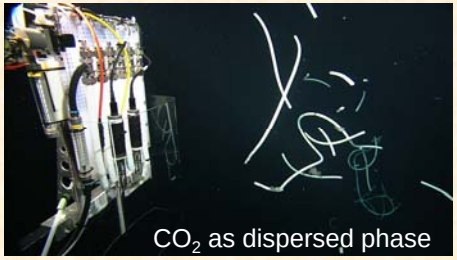
Battery of four CJHR in series

CO_2 load = 30 g/s

Depth = 1200 – 2000 m

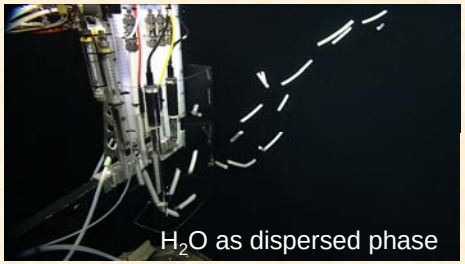


Sequestering CO_2 with the CJHRs

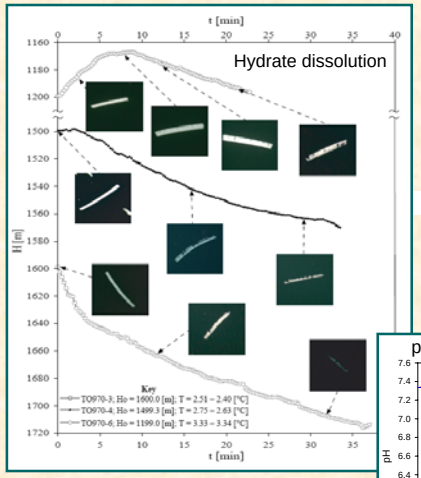


Production of consolidated, sinking hydrate particles at intermediate ocean depths (1200 – 2000 m)

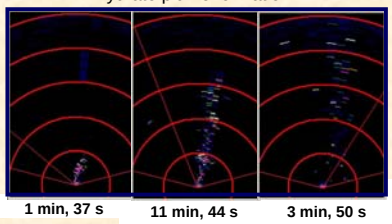
- H_2O as dispersed phase more effective in the field
- Plume of slowly dissolving particles (average life time 18 min)
- Maximum pH increase at injection point = 0.15



Valuable information obtained from the field

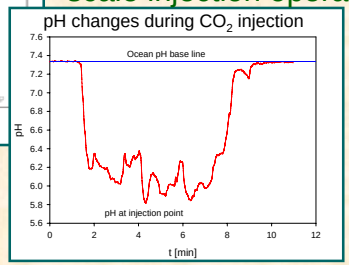


Hydrate plume formation



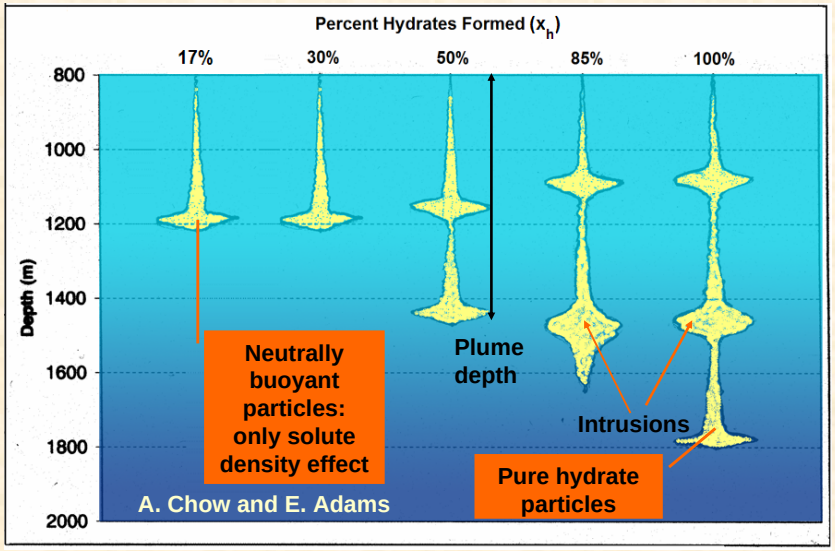
Sonars:
1500 m
8 m/div

Plume modeling ⇒ assessment of feasibility and impact of large-scale injection operations



Hydrate behavior in the ocean: plume modeling

(100 kg/s CO_2, 1 cm diameter spheres, release depth 800 m, $Q_c/Q_w = \lambda = 0.49$)



Conclusions

- Design, construction, and testing of a pilot scale CJHR: produces solid, denser than water, composite particles
- Key component for success: increase in interfacial area between reactants
- Thermal effects: important and more difficult to control than mass transfer barriers
- Successful field CO_2-injection with the CJHR

Acknowledgments

- Office of Biological and Environmental Research
- Monterey Bay Aquarium Research Institute

Field Experiment, Monterey Bay (April, 2006)

Oak Ridge National Laboratory

MIT

MBARI

Fisheries and Oceans Canada

Department of Energy, United States of America