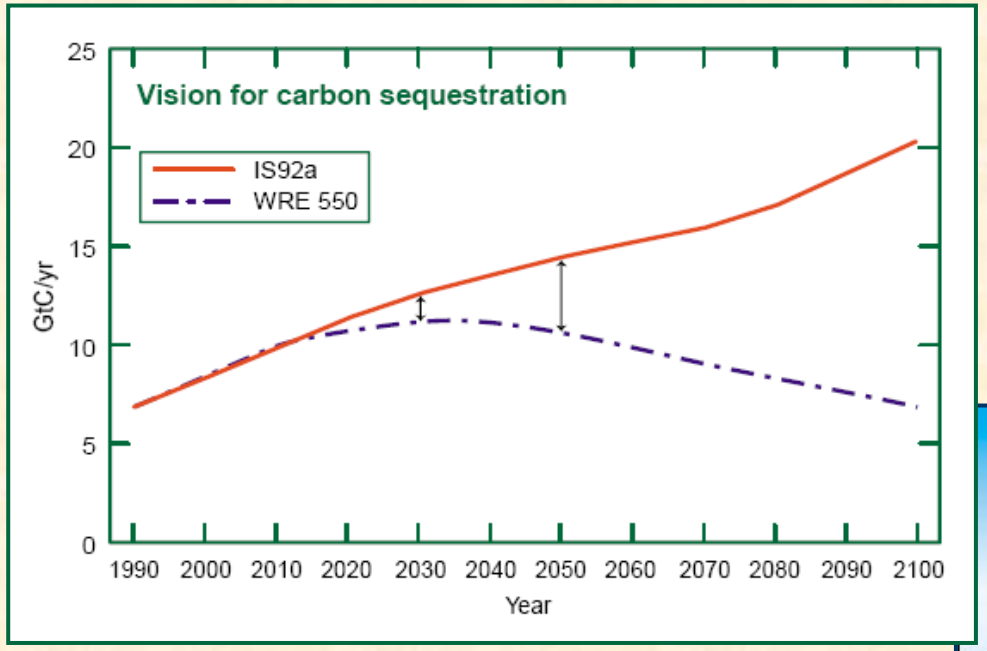
Process Intensification and Innovation Process $(PI)^2$
September 24 – 29, 2006
Christchurch, New Zealand

Continuous-Jet Hydrate Reactor

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

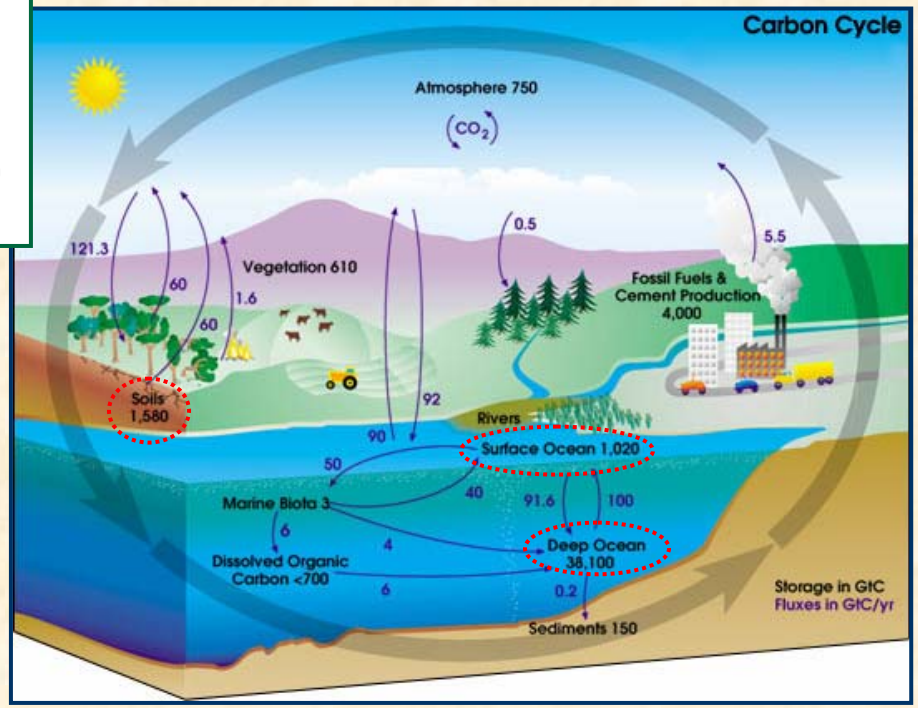
Greenhouse gases – the challenge



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

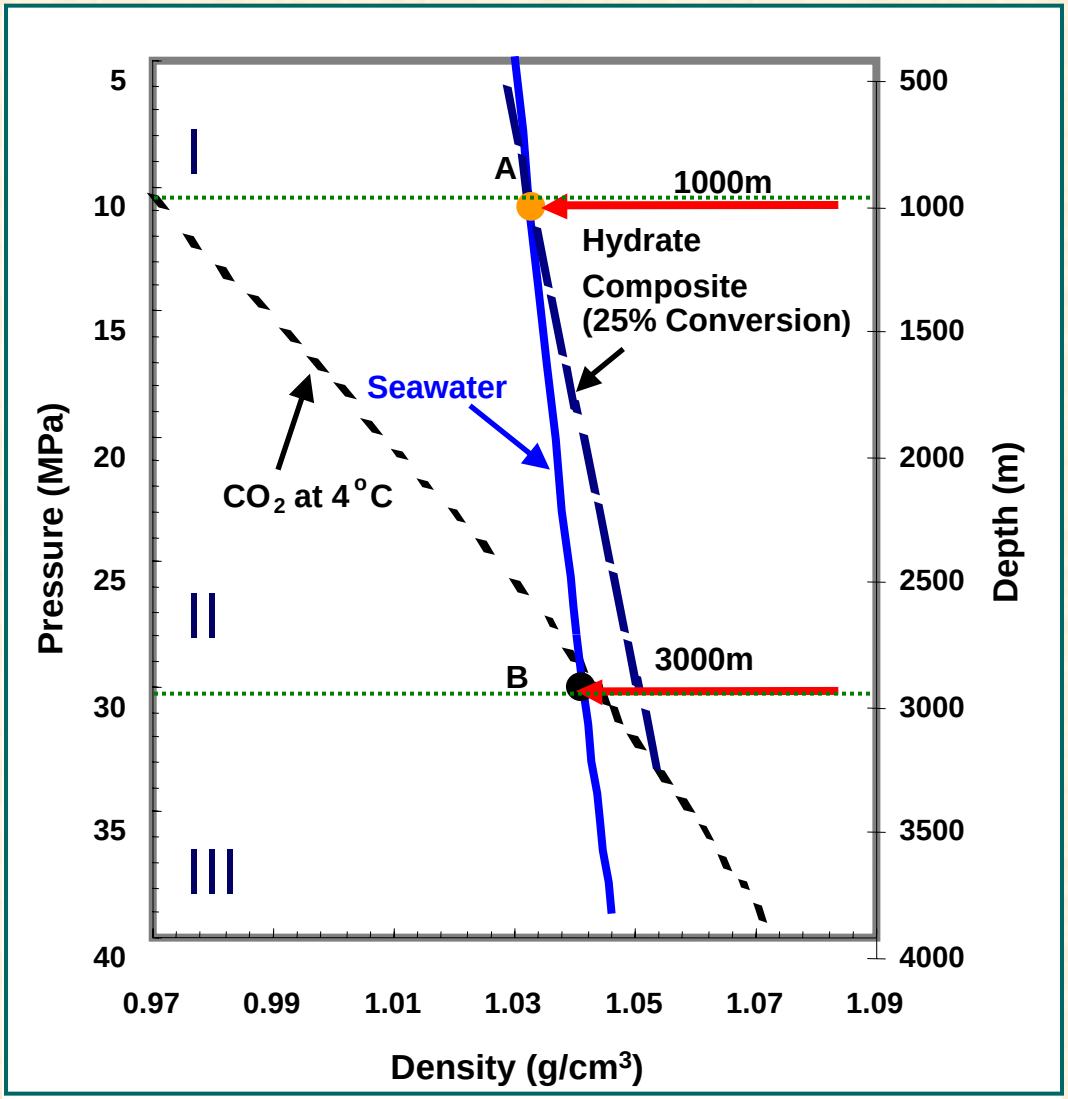
IS92a ⇒ "business as usual" or global warming

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)

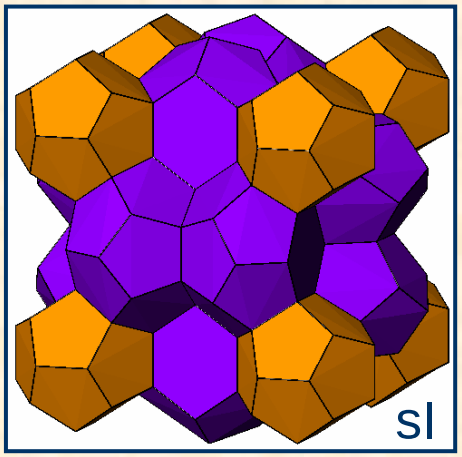
Factors to consider:

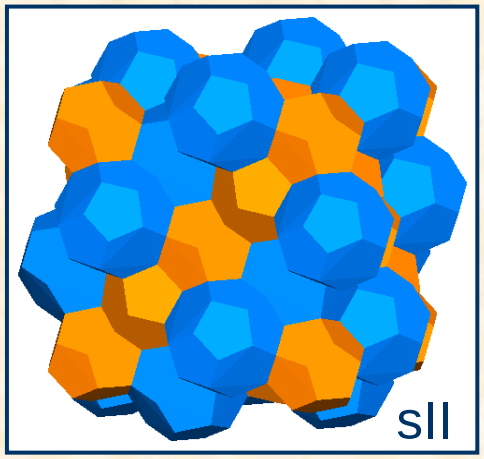
1. Environmental impacts
2. Residence time of carbon in the ocean
3. Operational costs

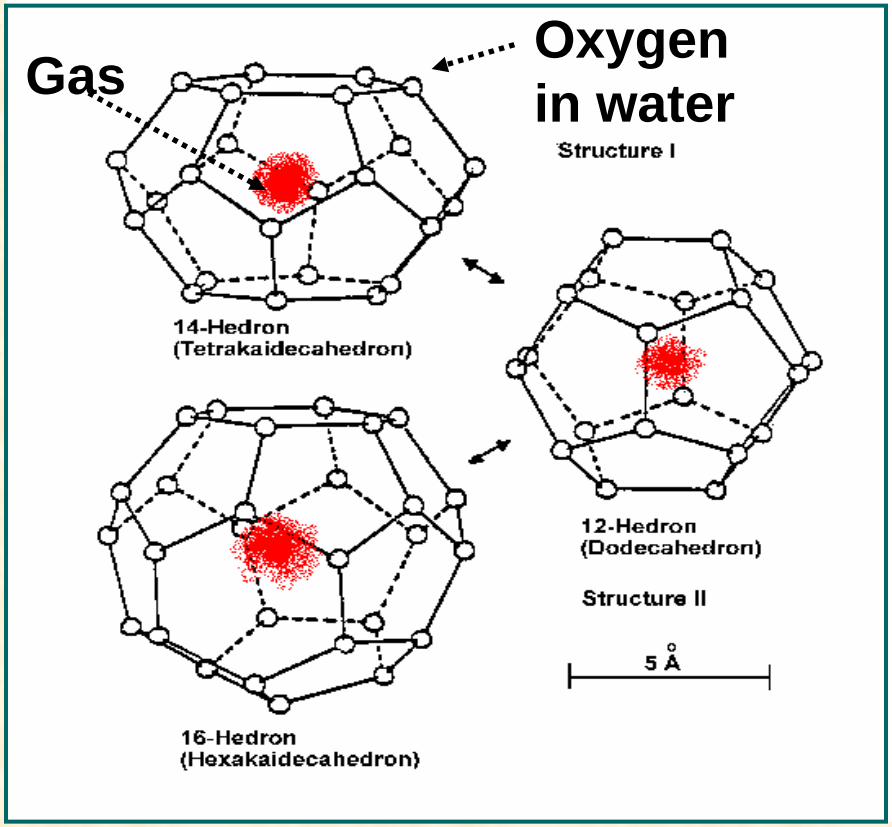
Adapted from Brewer et al., Science, 1999, **284**, 943 – 945.

CO_2 hydrate

Crystalline, ice-like structure stable at temperatures near 0 °C, and pressures above 0.113 MPa, with large CO_2 storage capacity







Individual hydrate cages combine to form sI or sII structures, depending on the host gas

CO_2 hydrate formation

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

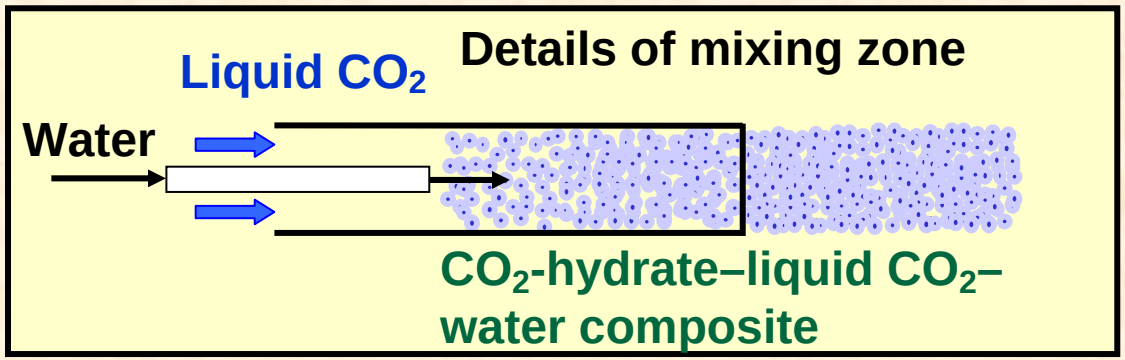
Instantaneous, exothermic reaction limited by:

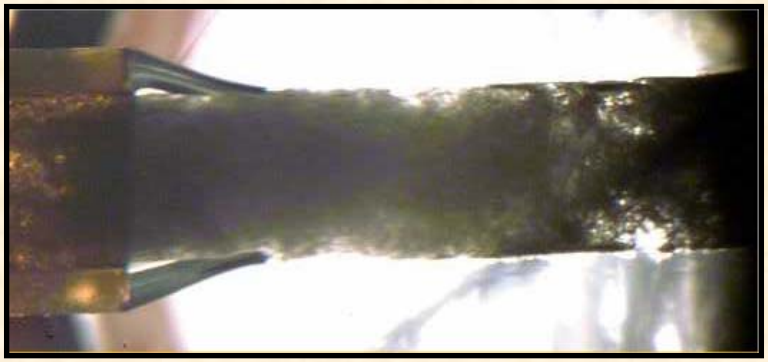
1. mass transfer barriers at the interface between reactants
2. dissipation rate of heat generated during reaction

CO_2-ocean sequestration purposes $\Rightarrow$ minimum conversion dictated by injection depth and temperature (typically 0.2)

$$x_{h_\min} = \frac{1/\rho_c - 1/\rho_w}{(1/\rho_c - 1/\rho_h) + 18n(1/\rho_w - 1/\rho_h)/44}$$

From laboratory- to pilot scale





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

Tubular reactor ⇒ vigorous mixing of reactants via injection of one into the other

<u>Laboratory-scale:</u>

CO_2 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

<u>Pilot-scale:</u>

CO_2 mass load: up to 10 g/s

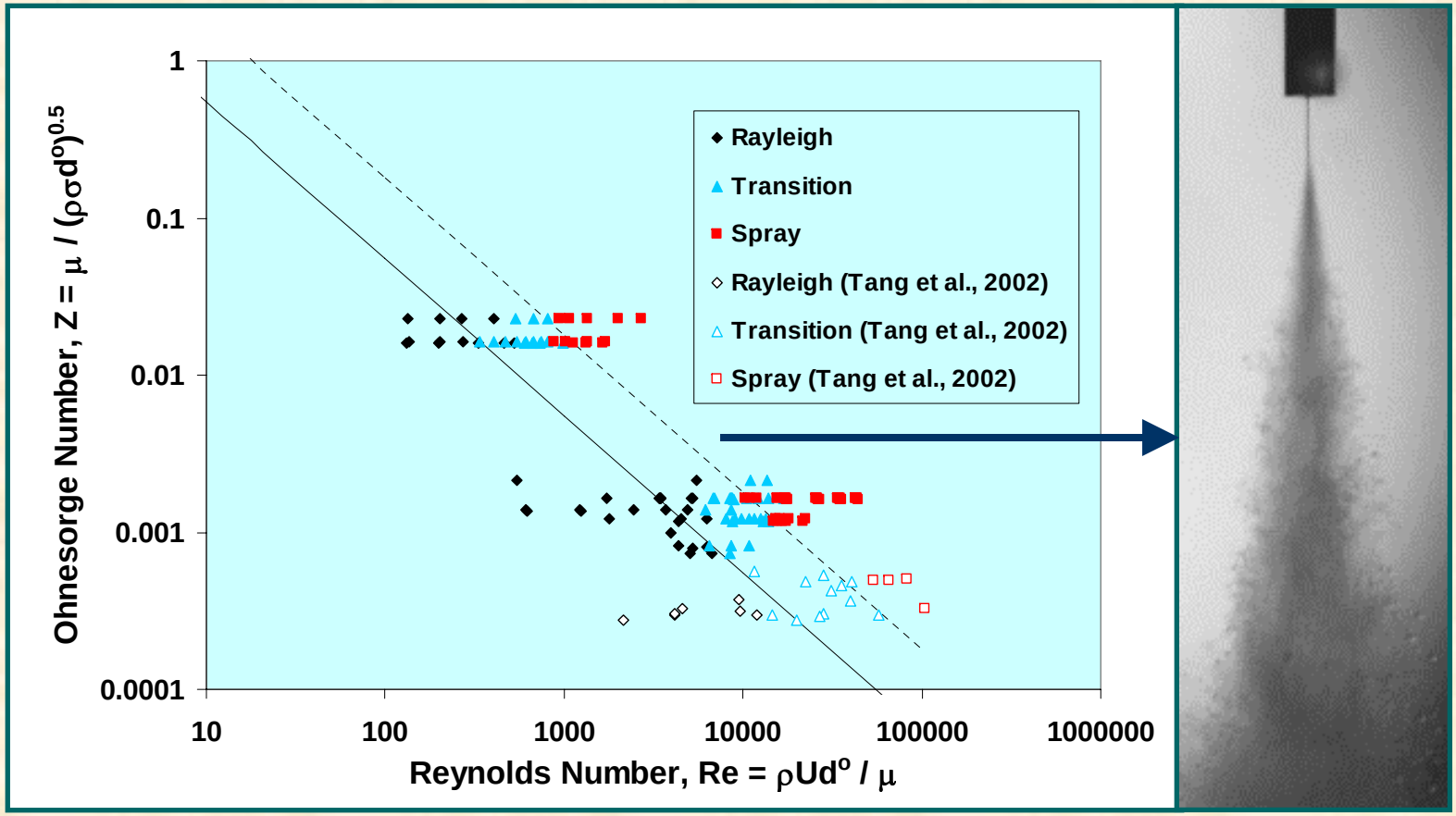
Conversion: > 0.20

Operation pressure: <13.0 MPa

Temperature = 2 – 6 °C

Diameter: 2.54 cm

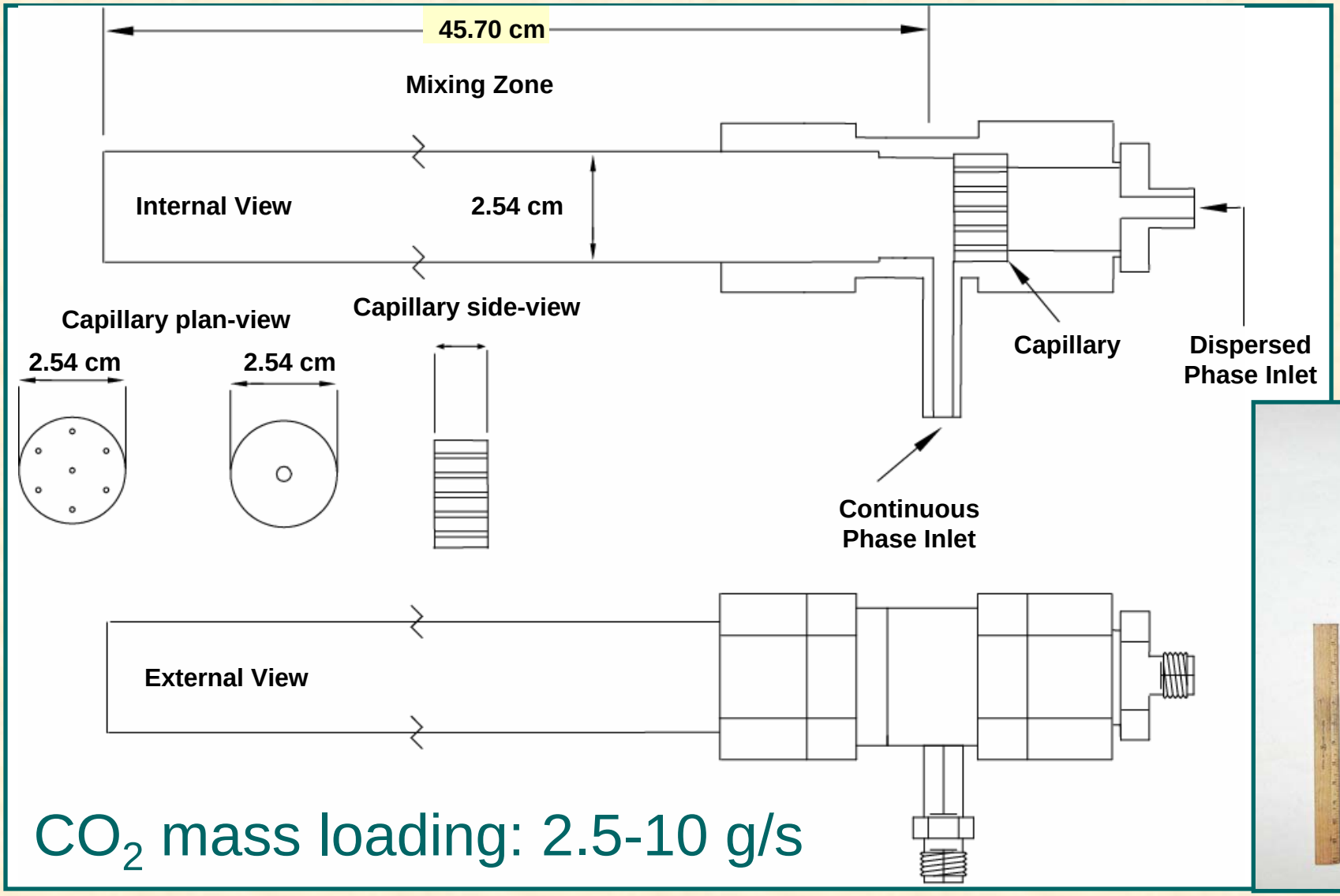
Design criterion for the pilot-scale reactor



Riestenberg et al., Amer. Mineral., 2004, **89**, 1240 – 1246.

Maximization of interfacial area between reactants to diminish mass transfer limitations and thermal effects

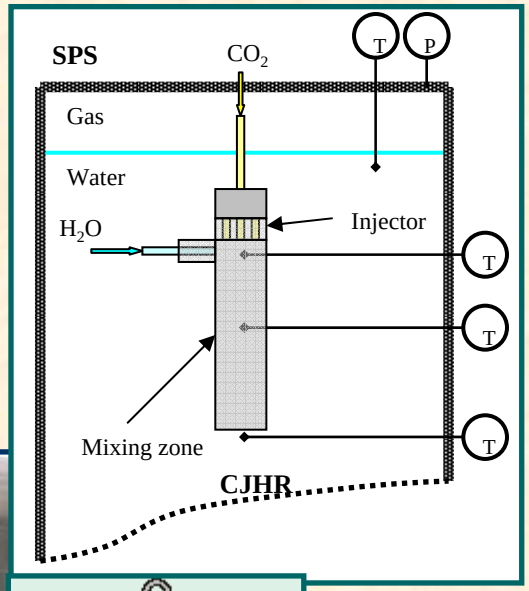
The continuous-jet hydrate reactor (CJHR)

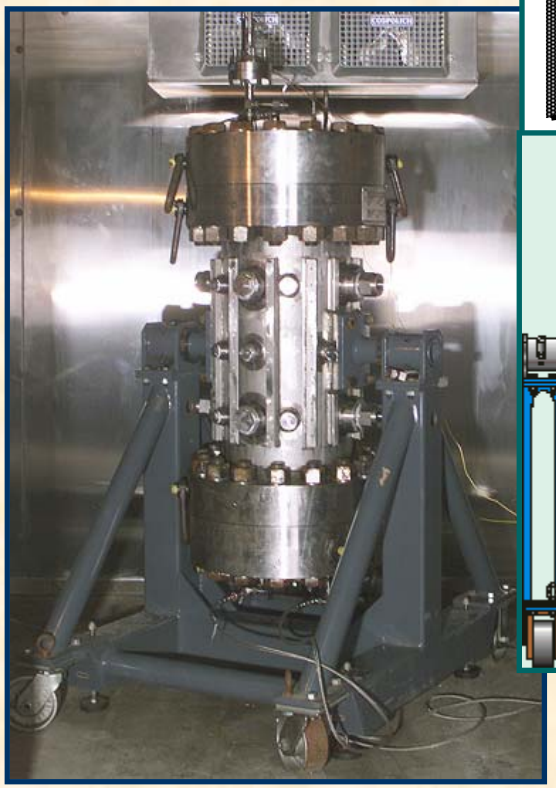


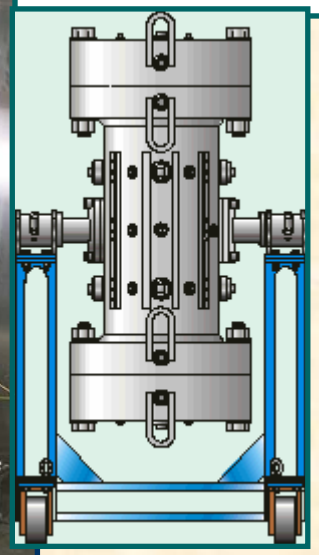
CO_2 mass loading: 2.5-10 g/s

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

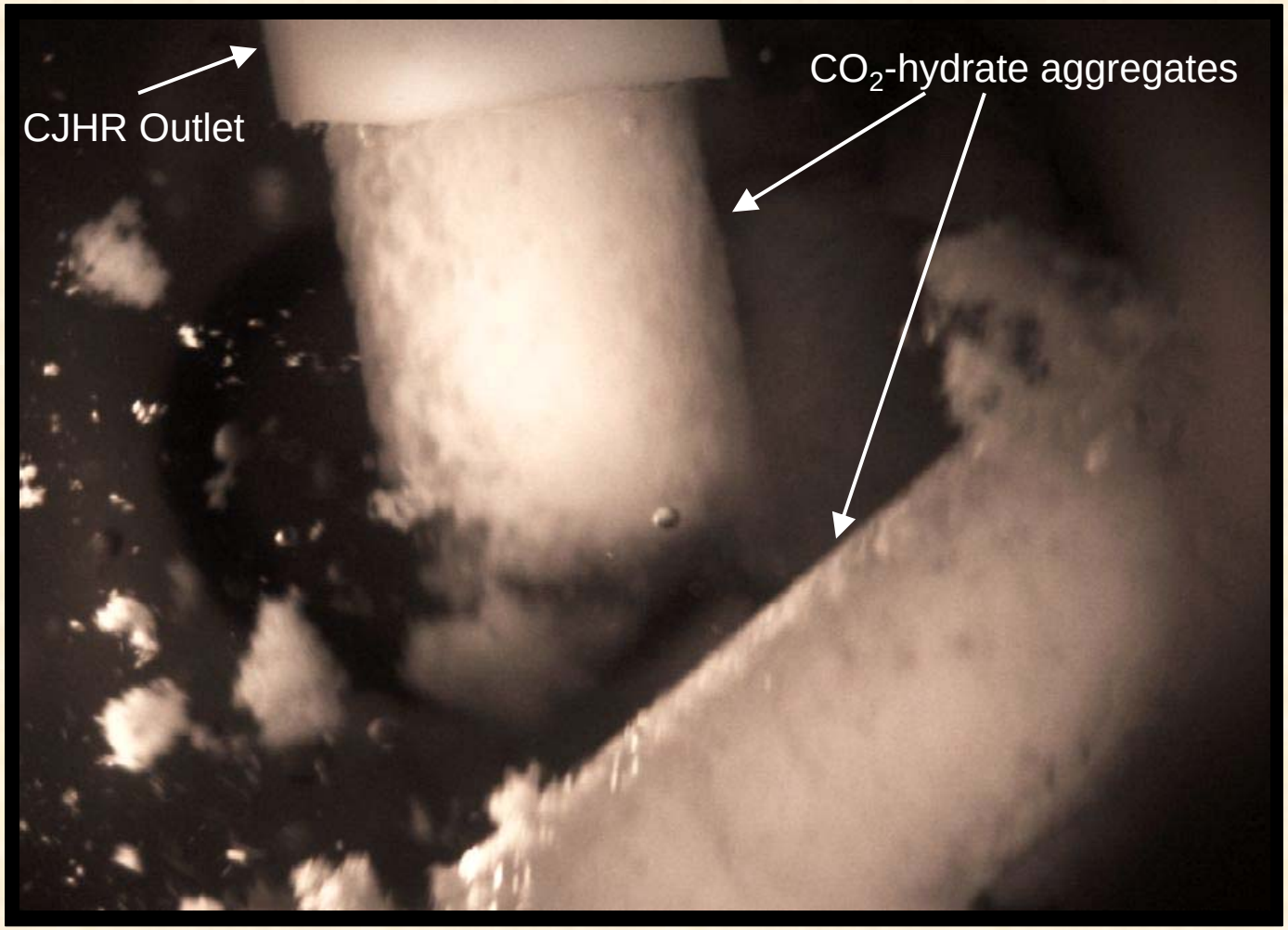




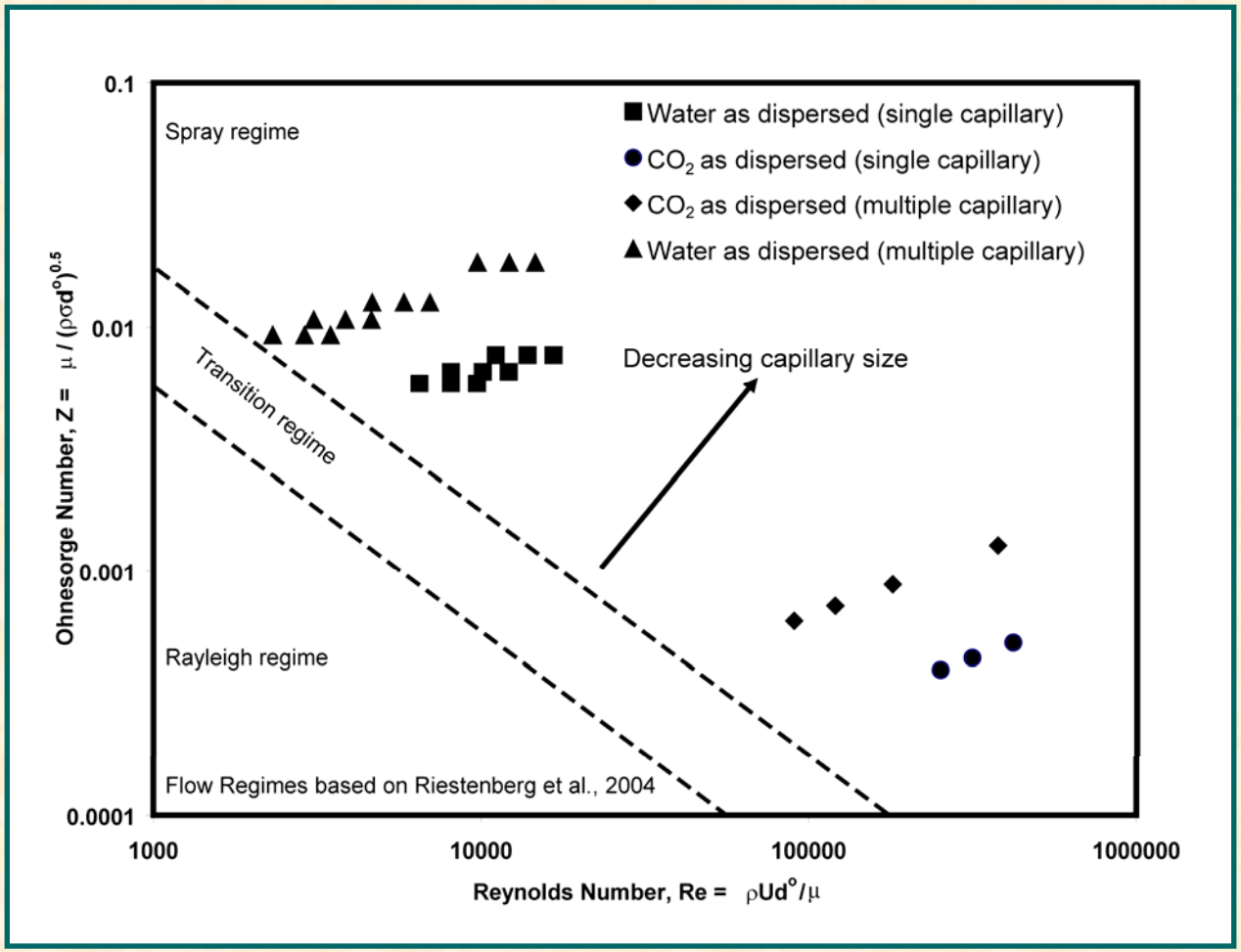


- Seafloor process simulator (SPS), a hastelloy vessel of 72 l
- Pressure and temperature monitoring
- Visualization

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 $\Rightarrow$ mixing conditions in spray regime

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_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 (~ 800 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

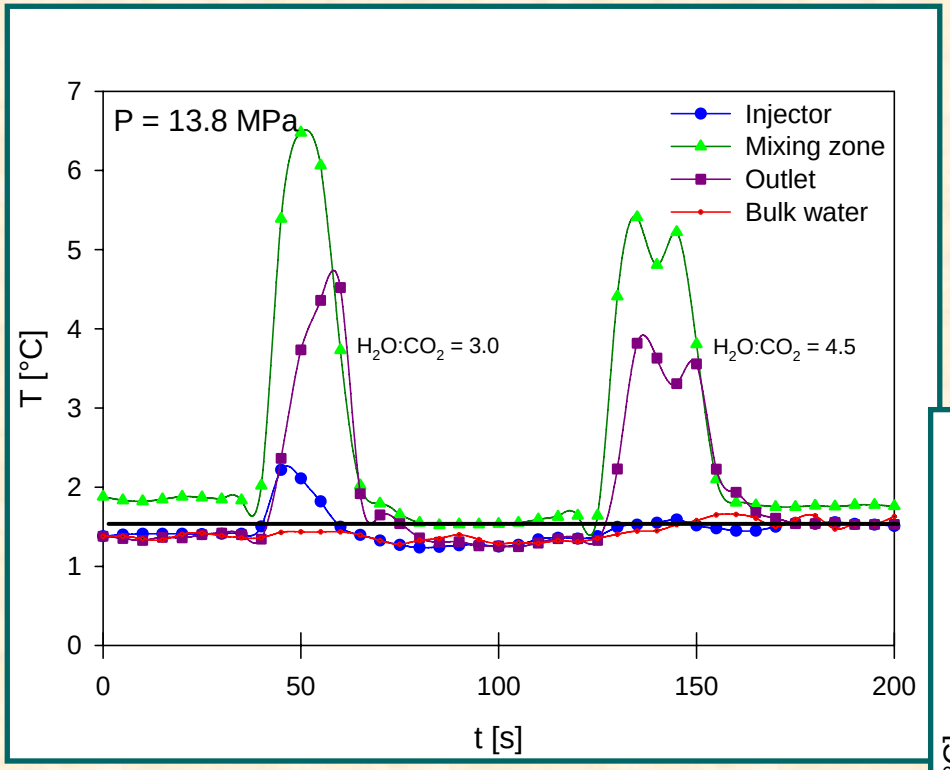
Seawater:

⇒ decrease in activity of water due to dissolved salt

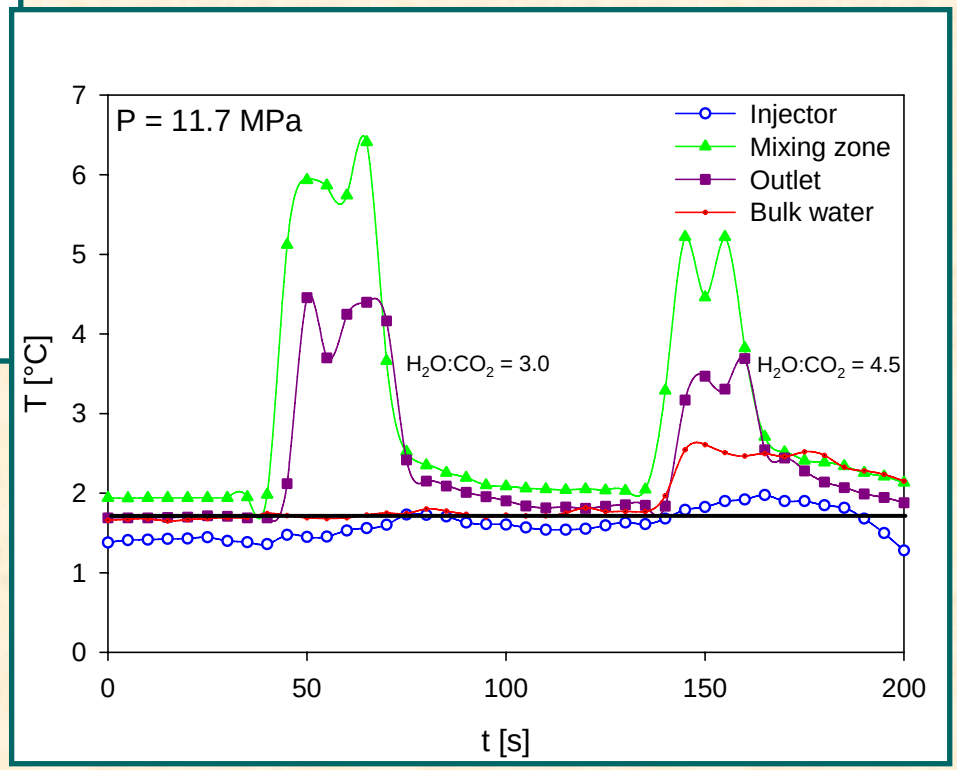
⇒ displacement of hydrate equilibrium towards lower T and higher P

Lower conversions in seawater ⇒ thermal effects?

Thermal effects

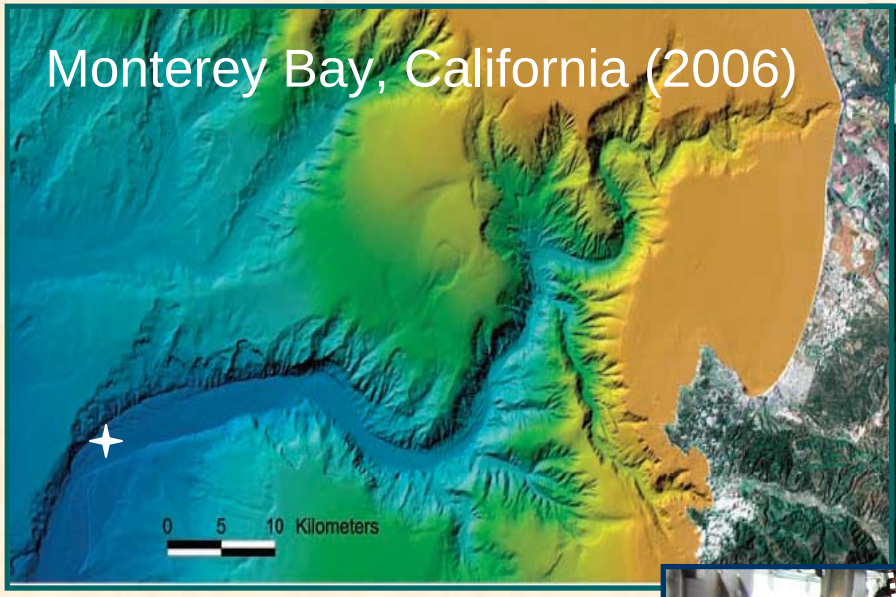


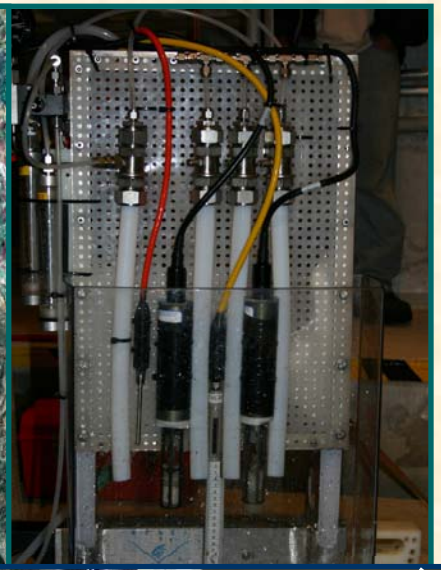
Local high T ⇒ local unfavorable thermodynamic conditions for hydrate formation



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

The CJHR in the field

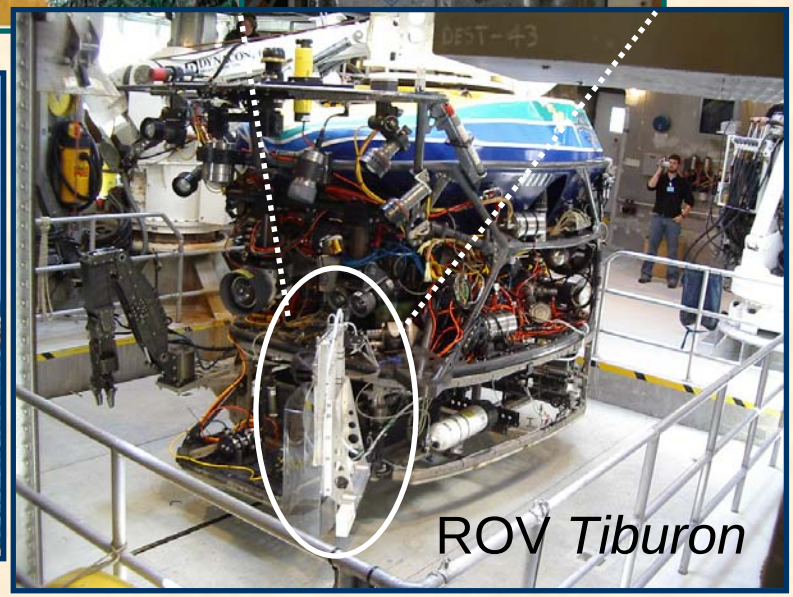




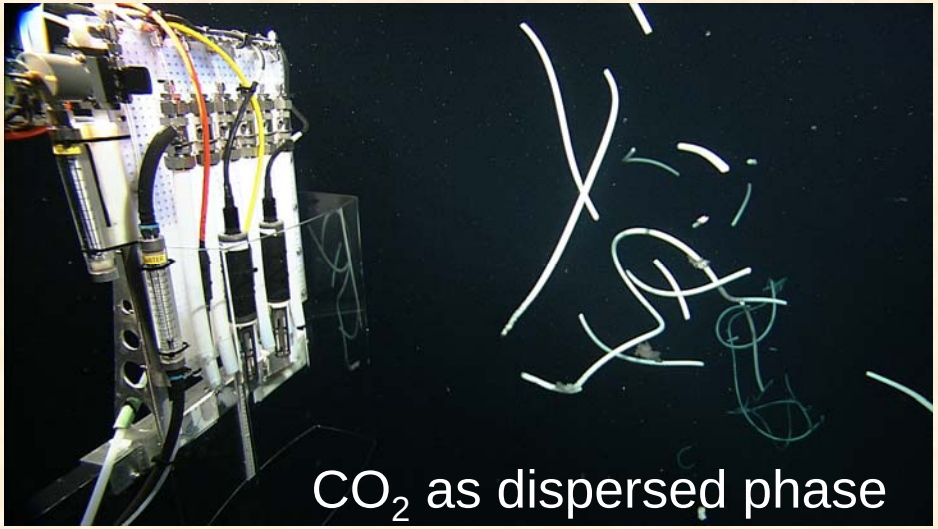
Battery of four CJHR in series

CO_2 load = 30 g/s

Depth = 1200 – 2000 m

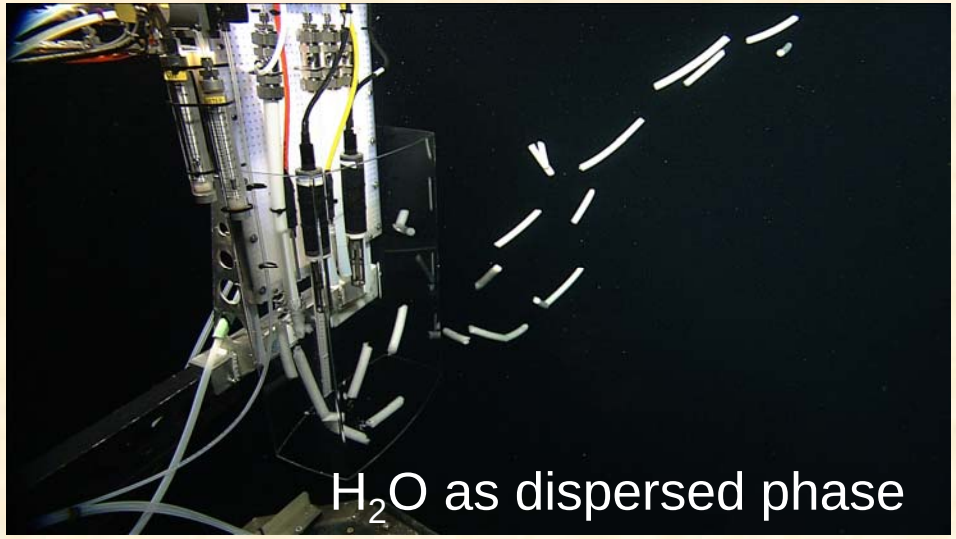


Sequestering CO_2 with the CJHRs

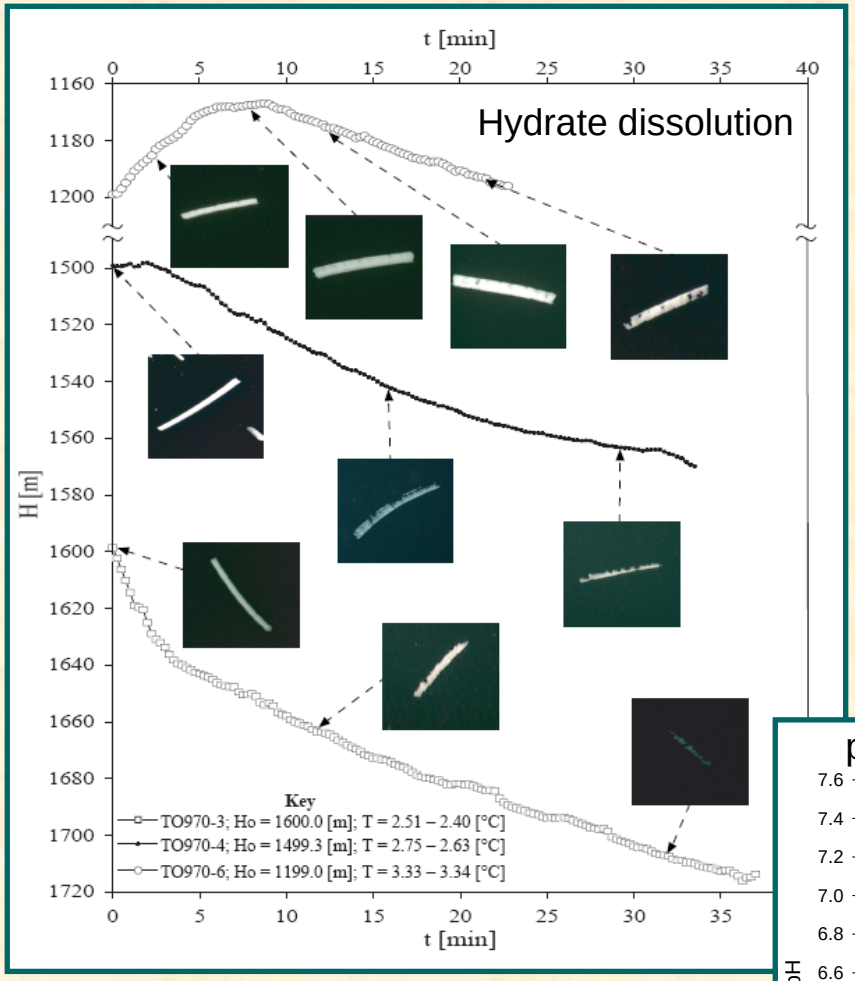


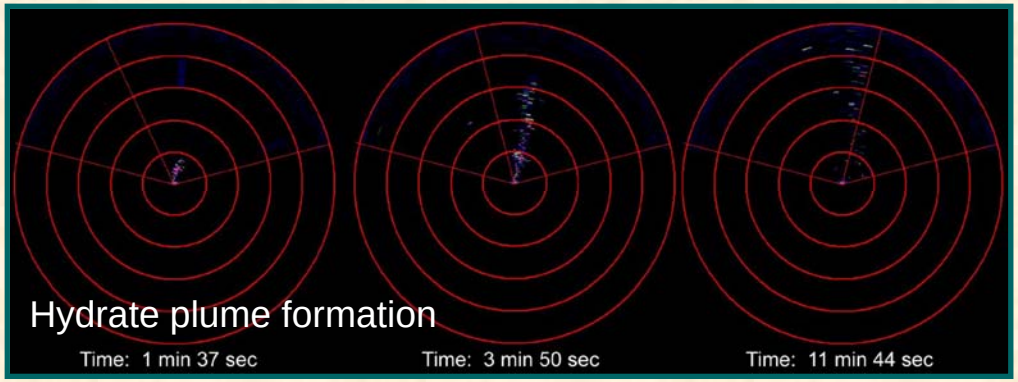
Production of consolidated, sinking hydrate particles at intermediate ocean depths (1200 – 2000 m)

- 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

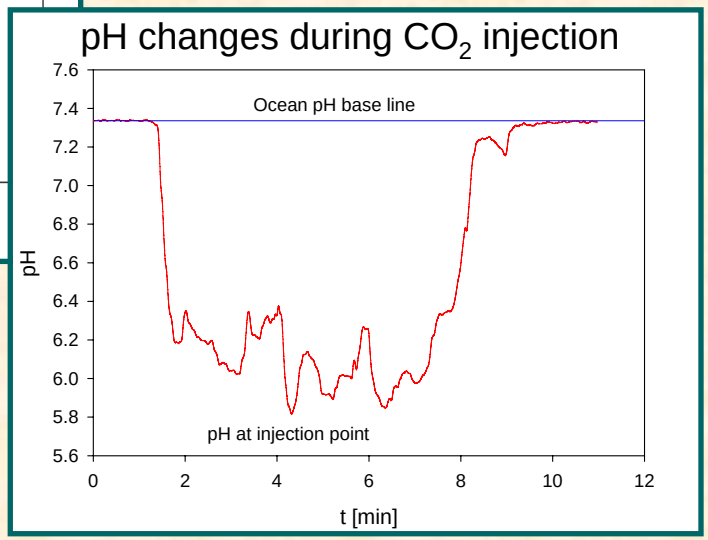


Valuable information obtained from the field





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



Relation to other reactors

- The CJHR has the characteristics of an intensified reactor
- It is compact and effective in producing high surface area and consolidated hydrate
- The residence time in the reactor is relatively small
- Its geometry allows effective heat transfer in the ocean
- A static mixer reactor does not produce consolidated hydrate, and does not allow good control of mixing
- A stirred-tank reactor that has been proposed by others would have several disadvantages

Conclusions

- Design, construction, and testing of a CJHR: more than ten-fold increase in production capacity, with increase in conversion and effectiveness
- 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, U.S. Department of Energy
- Peter Brewer, Monterey Bay Aquarium Research Institute
- Eric Adams, Massachusetts Institute of Technology