A Continuous-Jet Hydrate Reactor for the Formation of CO_2 Hydrate Particles: Hydrate Formation and Dissolution in a High-Pressure Water Tunnel Facility

C. Tsouris, D. Riestenberg, R. Warzinski,[1] R. Lynn,[1] S. McCallum, D. Aaron, J. Gabitto

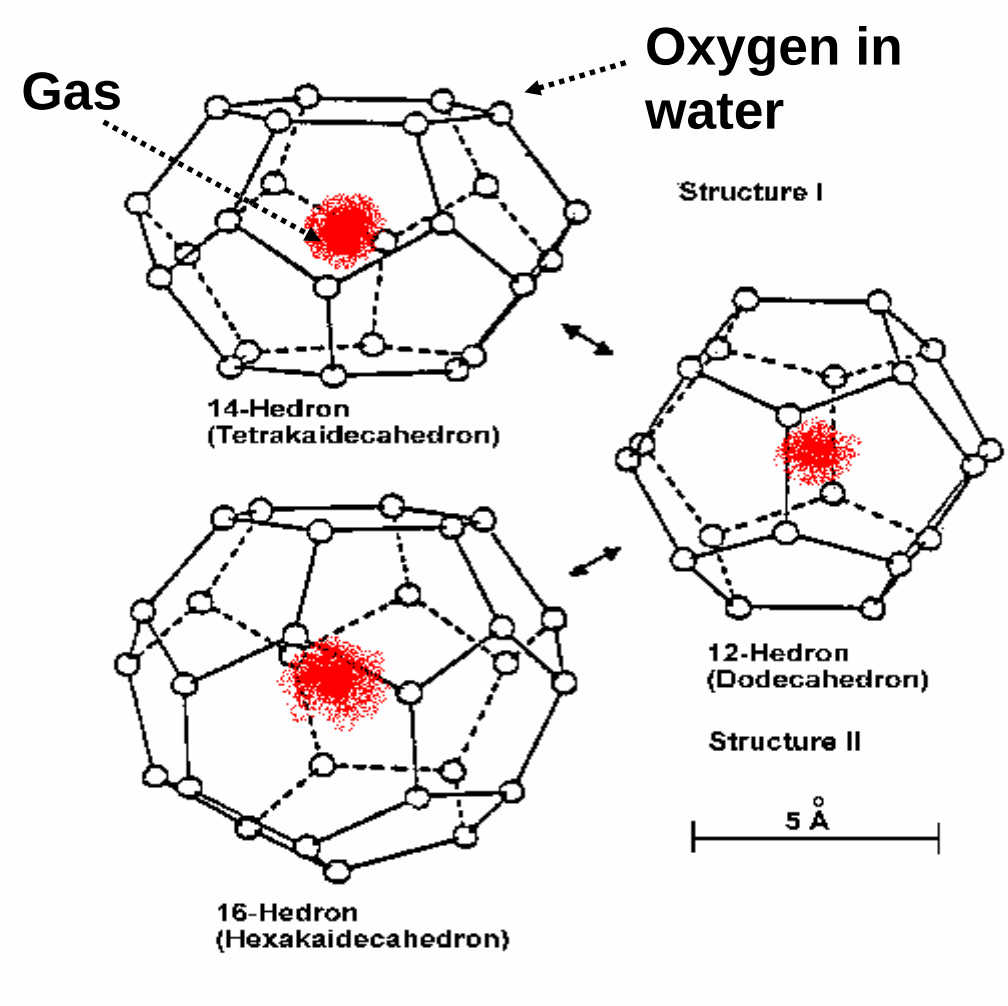
Oak Ridge National Laboratory
tsourisc@ornl.gov

[1]National Energy and Technology Laboratory
robert.warzinski@netl.doe.gov

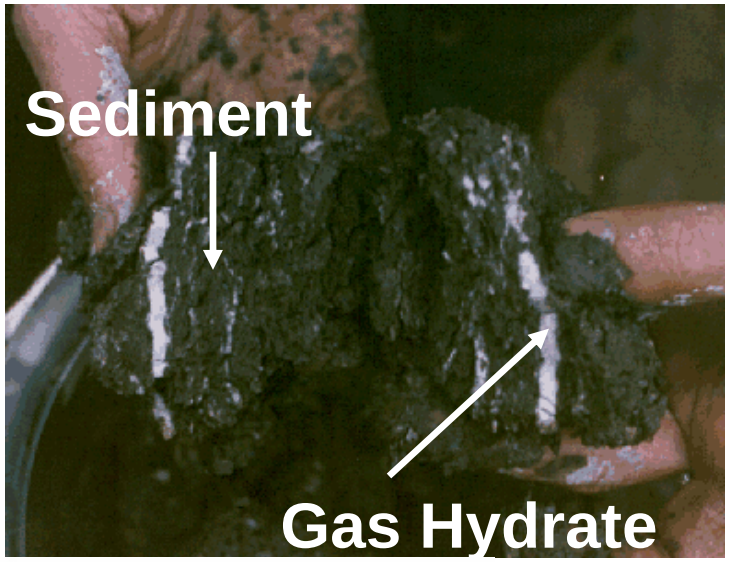
Why Studying Gas Hydrate Formation

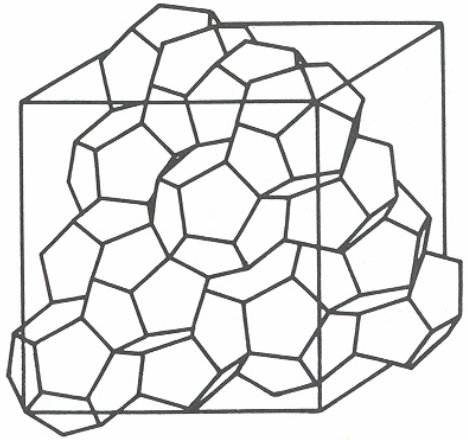
- Natural gas hydrates exist in ocean sediments and in permafrost
- They are considered a vast future energy source
- Gas hydrates form in gas pipelines causing clogging problems
- Here, we study formation and dissociation of CO_2 hydrate for the purpose of ocean carbon sequestration
- However, CO_2 hydrate can be used for diverse applications, including water purification and gas separations

Gas Hydrate Structure



Individual Cages

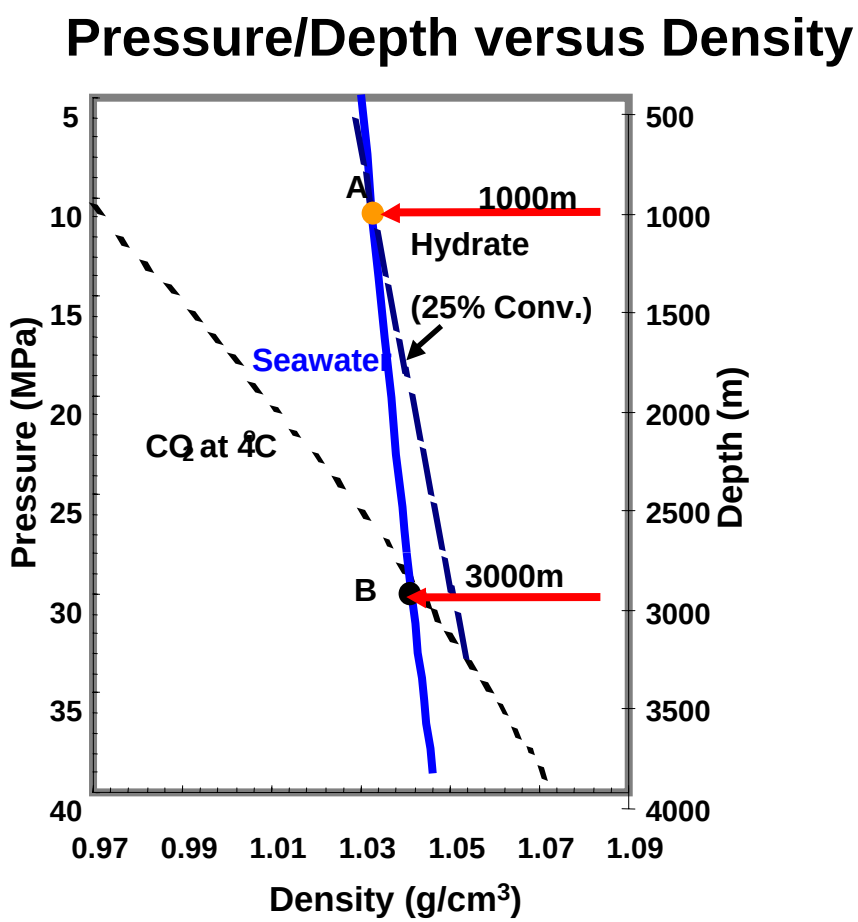


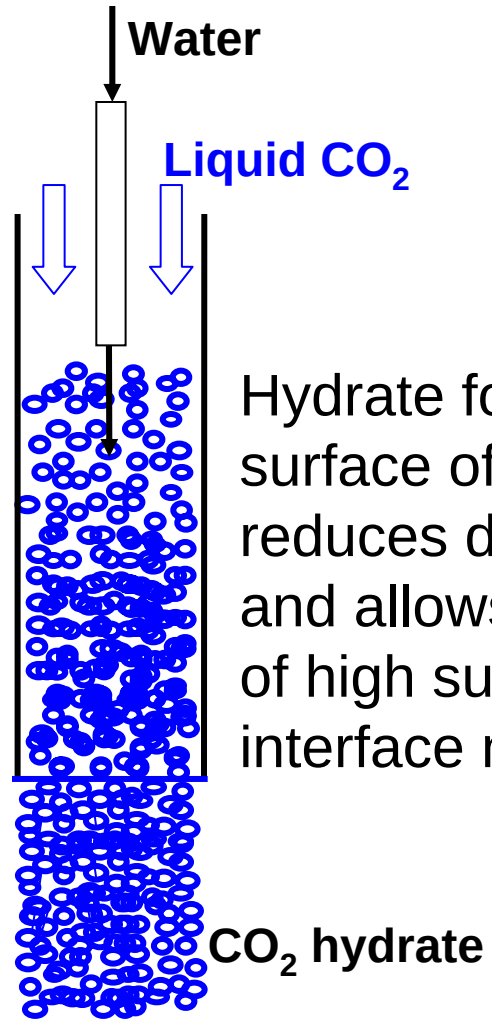


Unit Cell (Structure II)

Concentration of Gas: 164 m^3 CH_4 gas per m^3 CH_4 hydrate

Concept for CO_2 Hydrate Formation



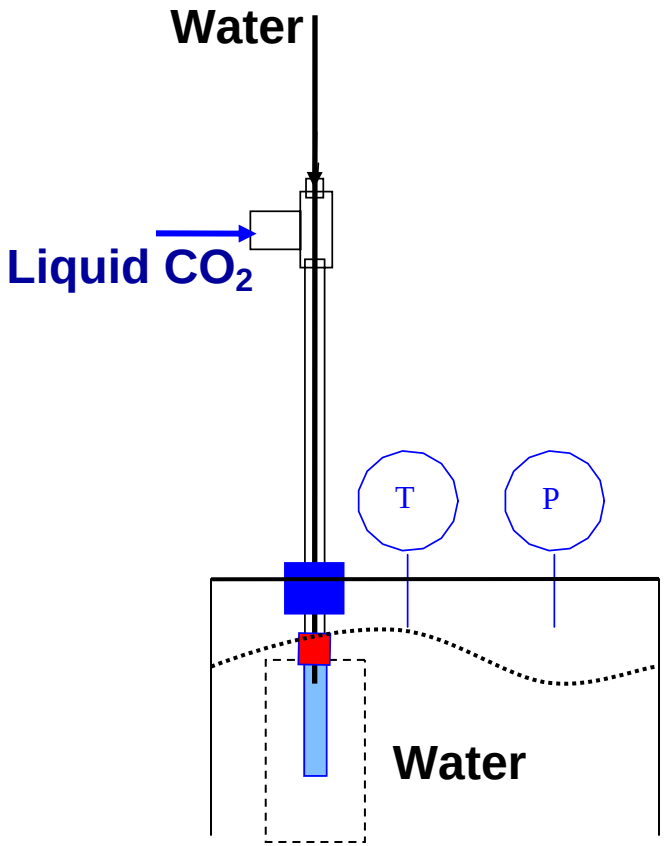


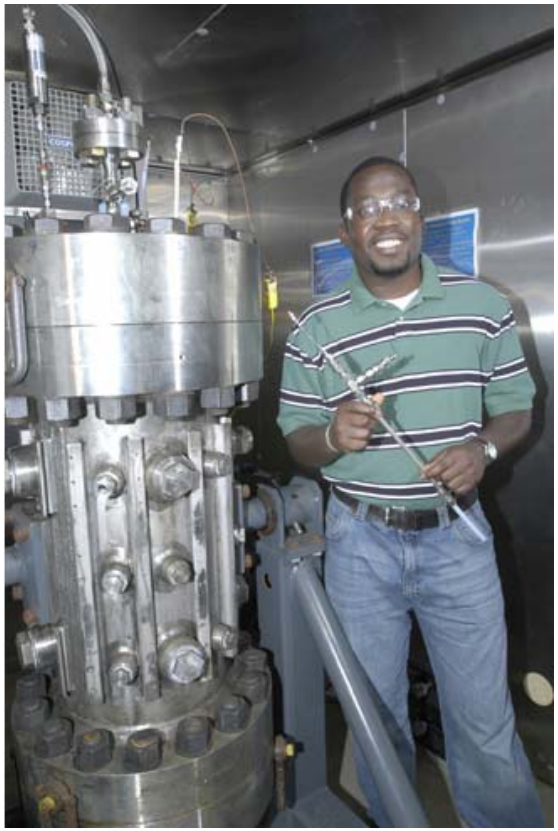
Hydrate formation on the surface of droplets reduces drop coalescence and allows the formation of high surface area for interface mass transfer

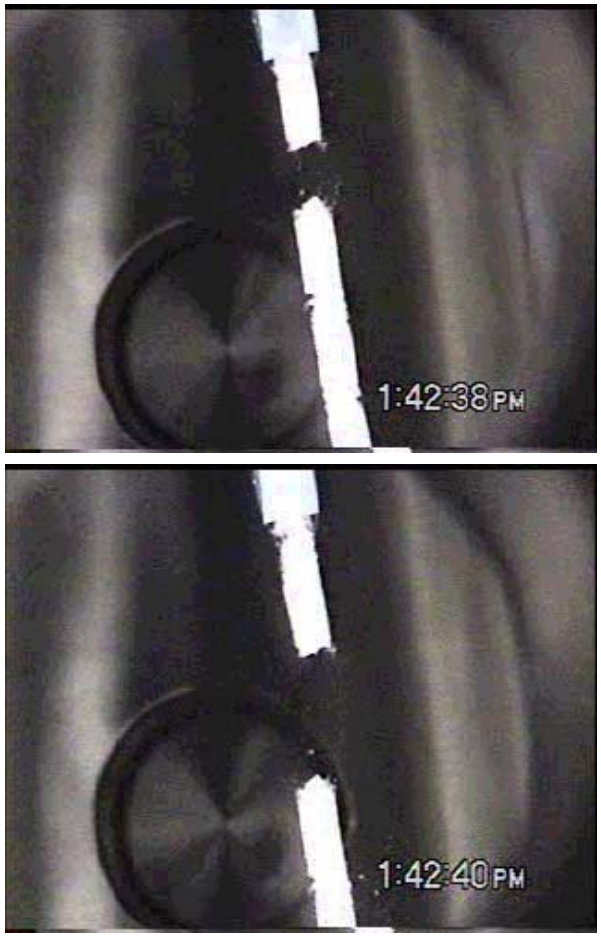
The density of the solid produced depends highly on the conversion of liquid CO_2 to hydrate.

West et al., AIChE J., 2003

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





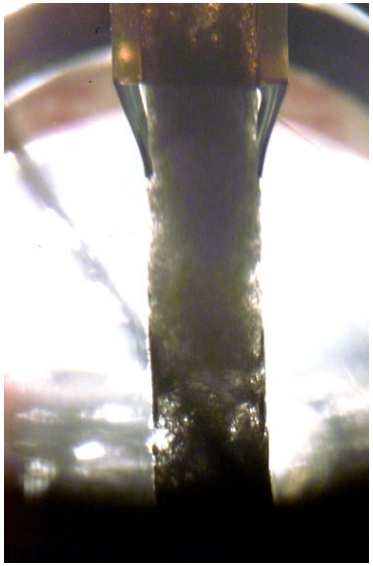


(72-L high pressure vessel)

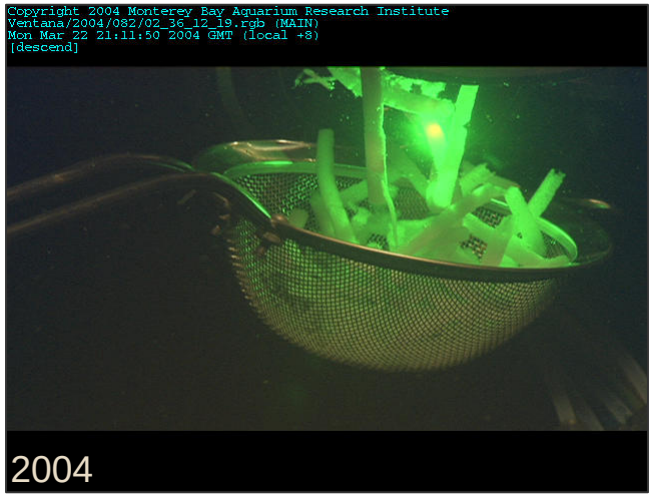
Formation of dense CO_2 hydrate composite was demonstrated in the laboratory using the CJHR reactor.

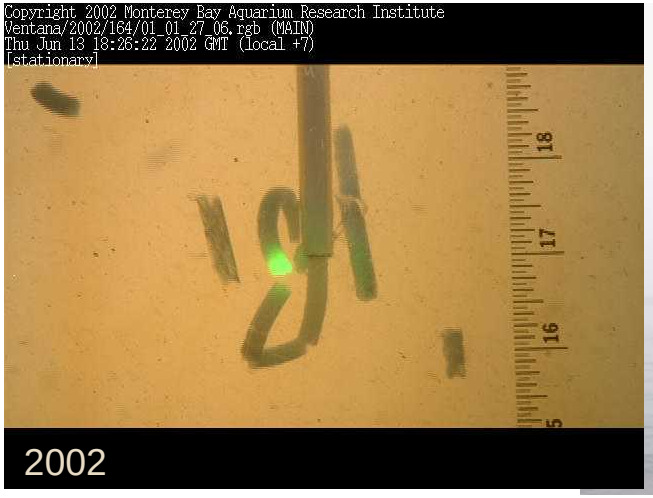
Lee et al., ES&T, 2003

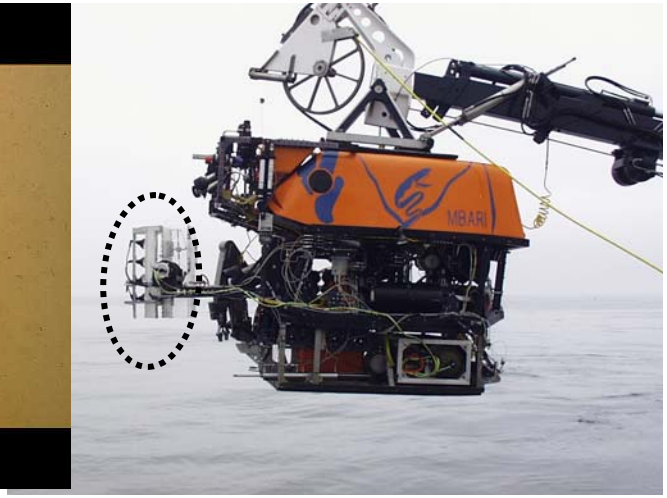
From the Laboratory to the Field



(Installation of ORNL injector with Raman spectrometer)



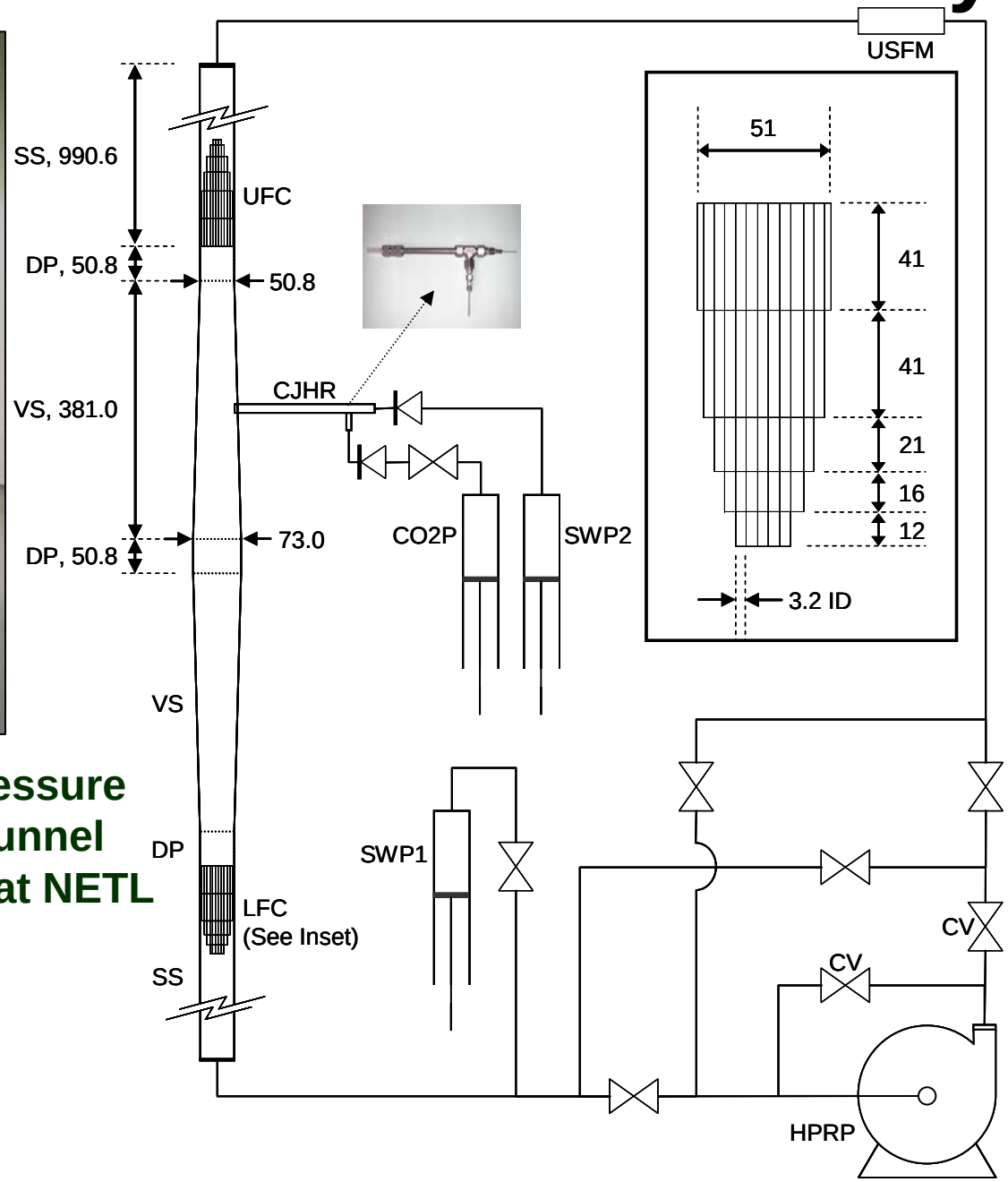




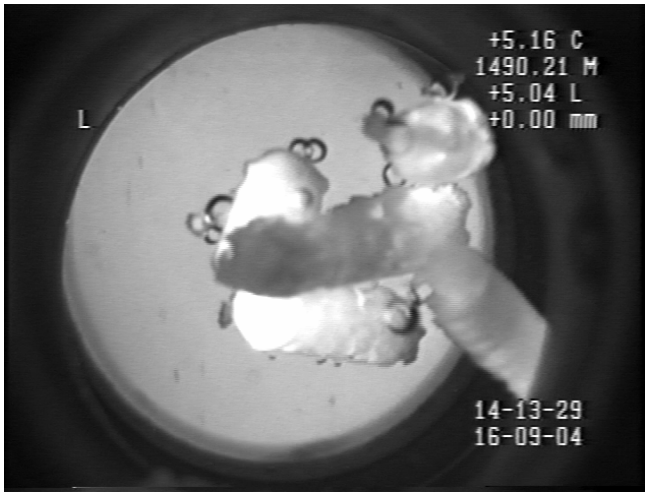
Tsouris et al., ES&T, 2004; Riestenberg et al., ES&T, 2005

From the Field to the NETL-HWTF Facility

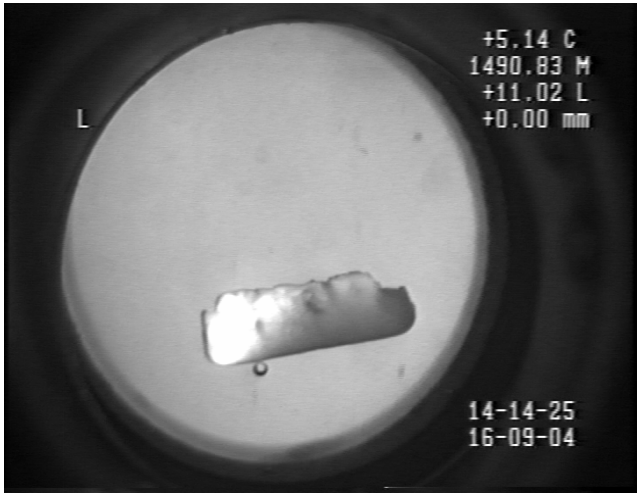
High-Pressure Water Tunnel Facility at NETL



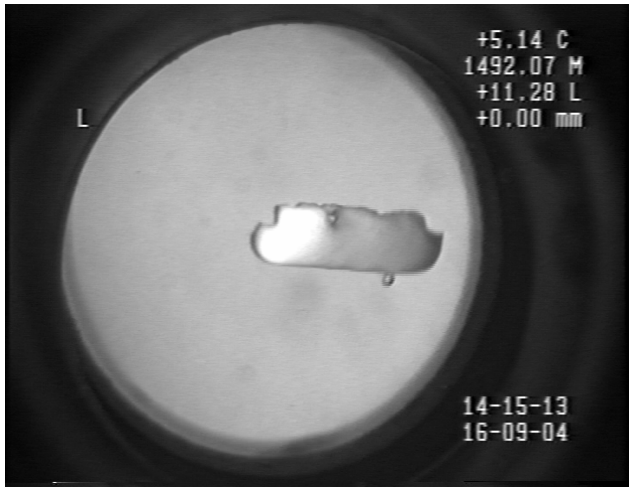
Time-Series Images of Sinking CO_2 Hydrate Composite Particles



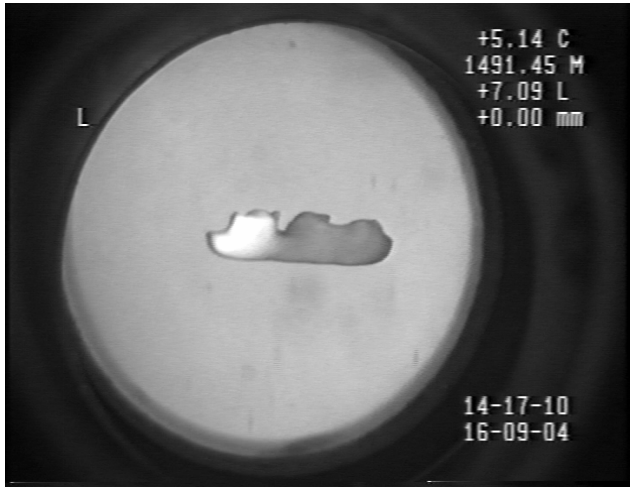
Elapsed Time, t = 103 s



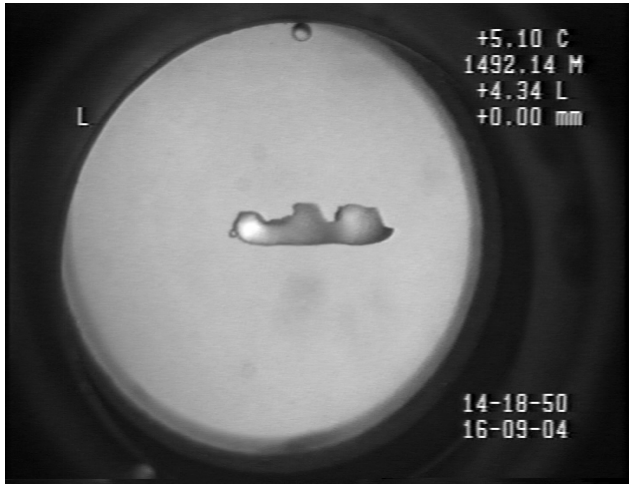
t = 157 s



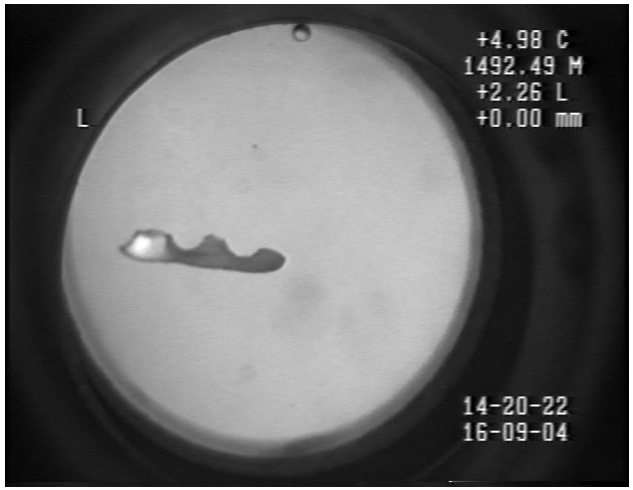
t = 205 s



t = 322 s

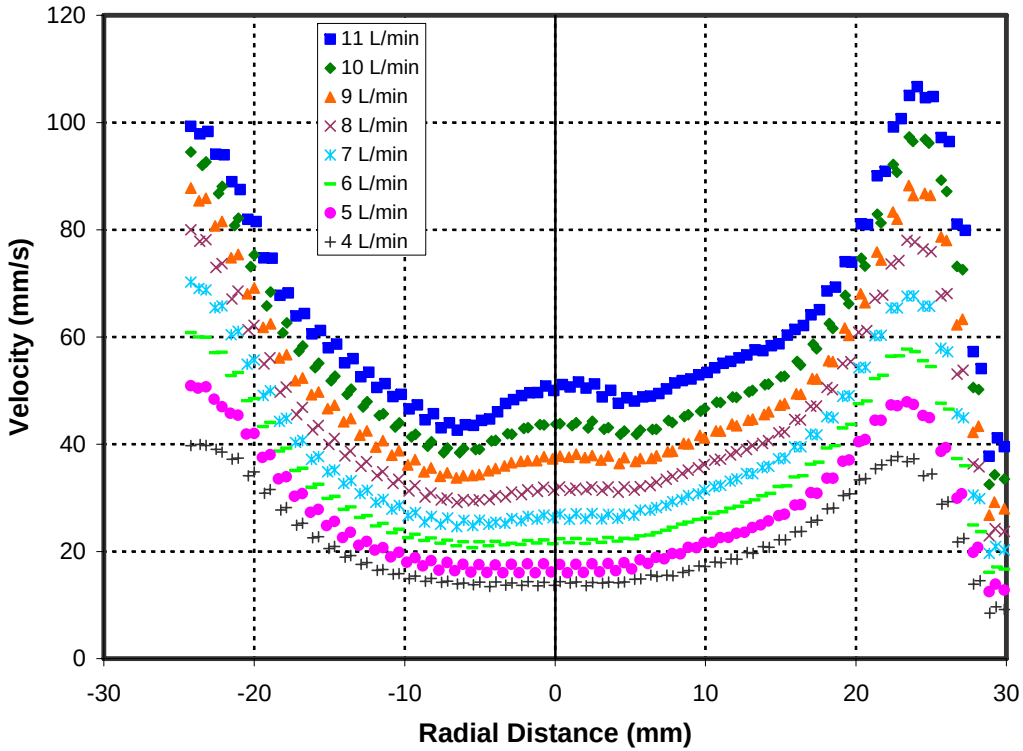


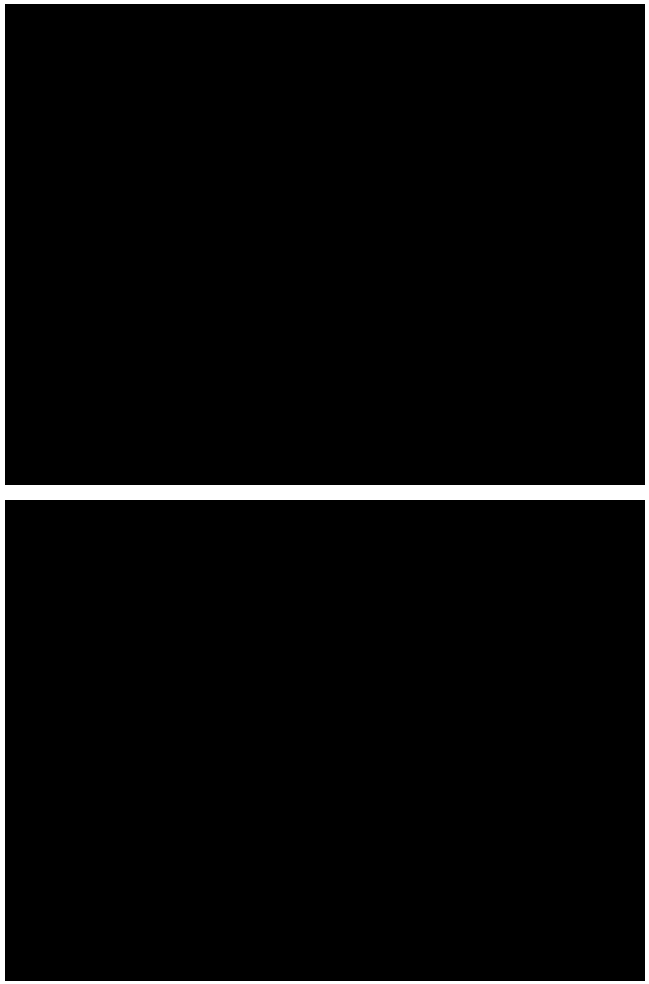
t = 422 s



t = 514 s

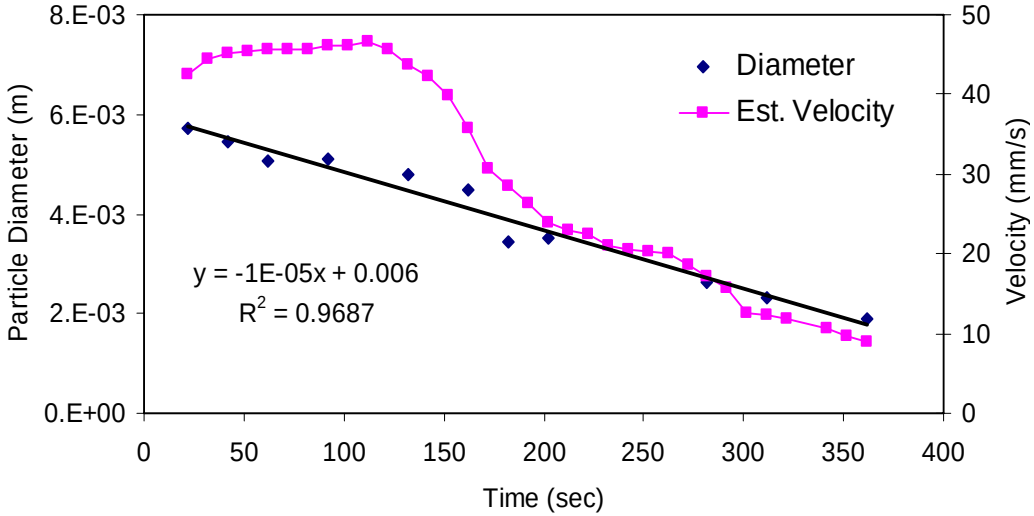
Velocity Profiles Produced in the Center of the Viewing Section by the Lower Flow Conditioner

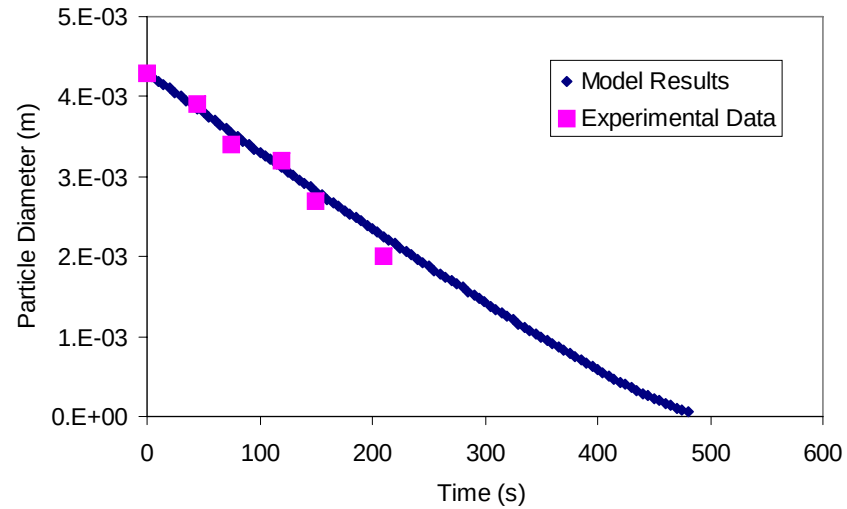


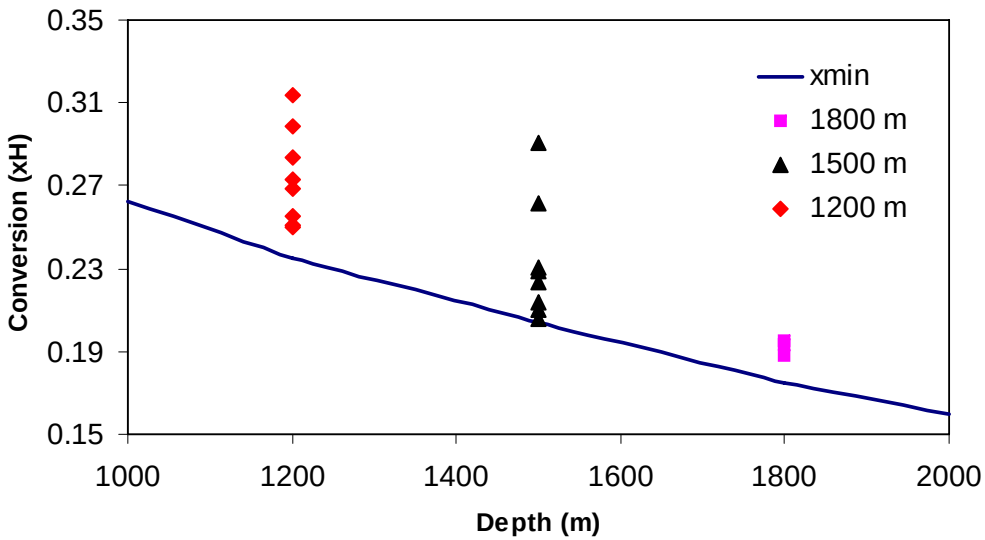


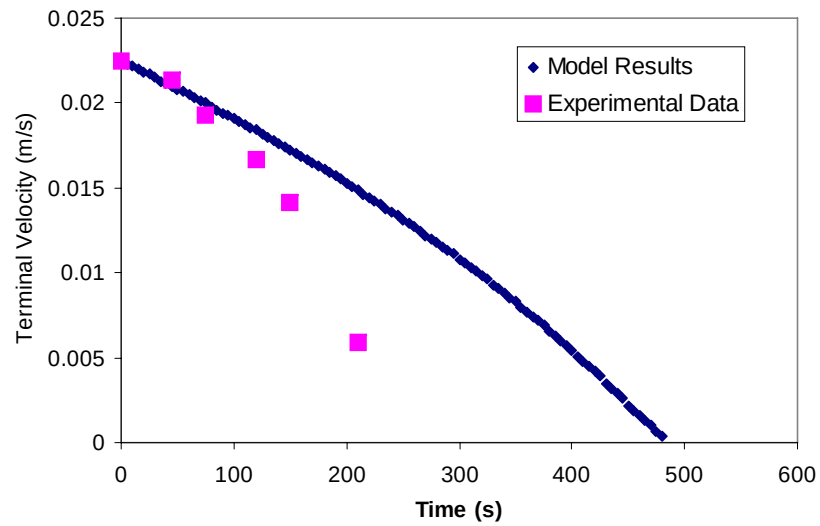
CO_2 hydrate composite particles are levitated in the HWTF allowing particle velocity and size measurements with time.

Experimental Data Obtained from HWTF and Comparison with Modeling Results





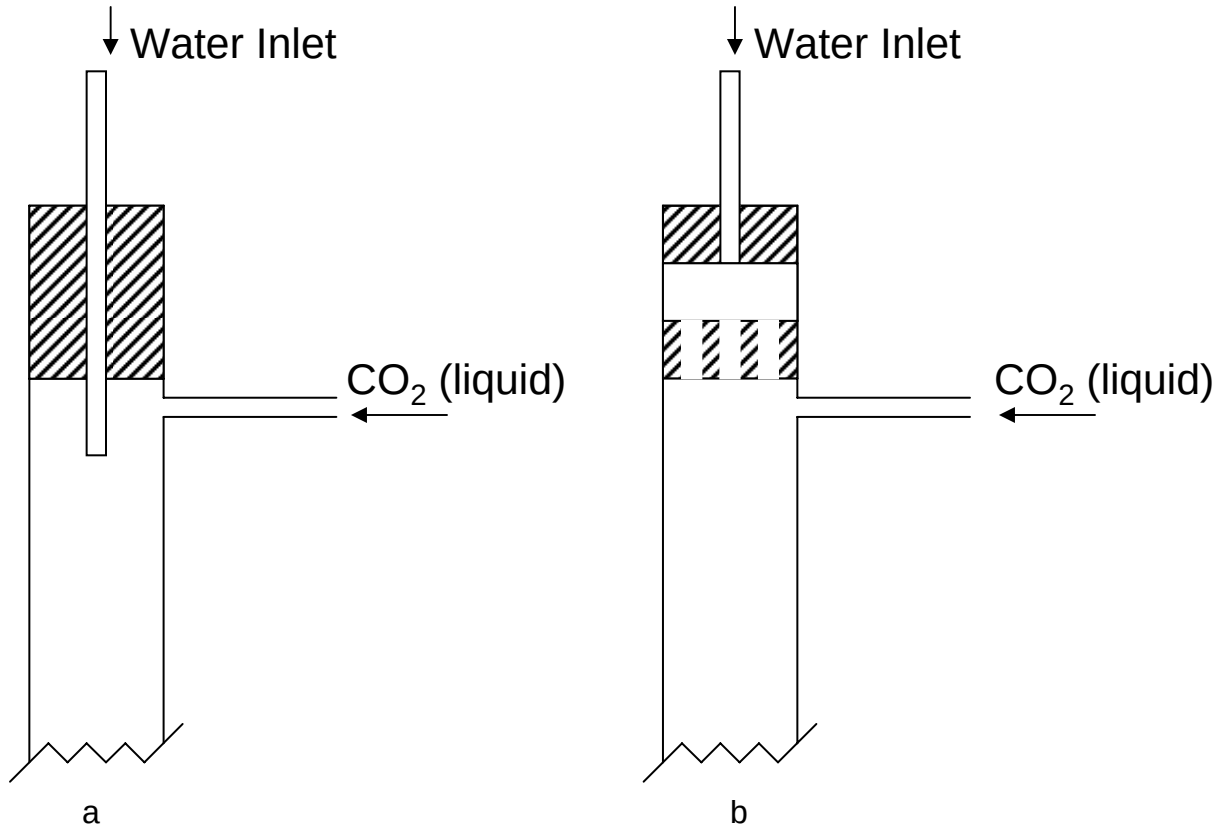




Injections at 1200-1800 m

Riestenberg et al., in preparation

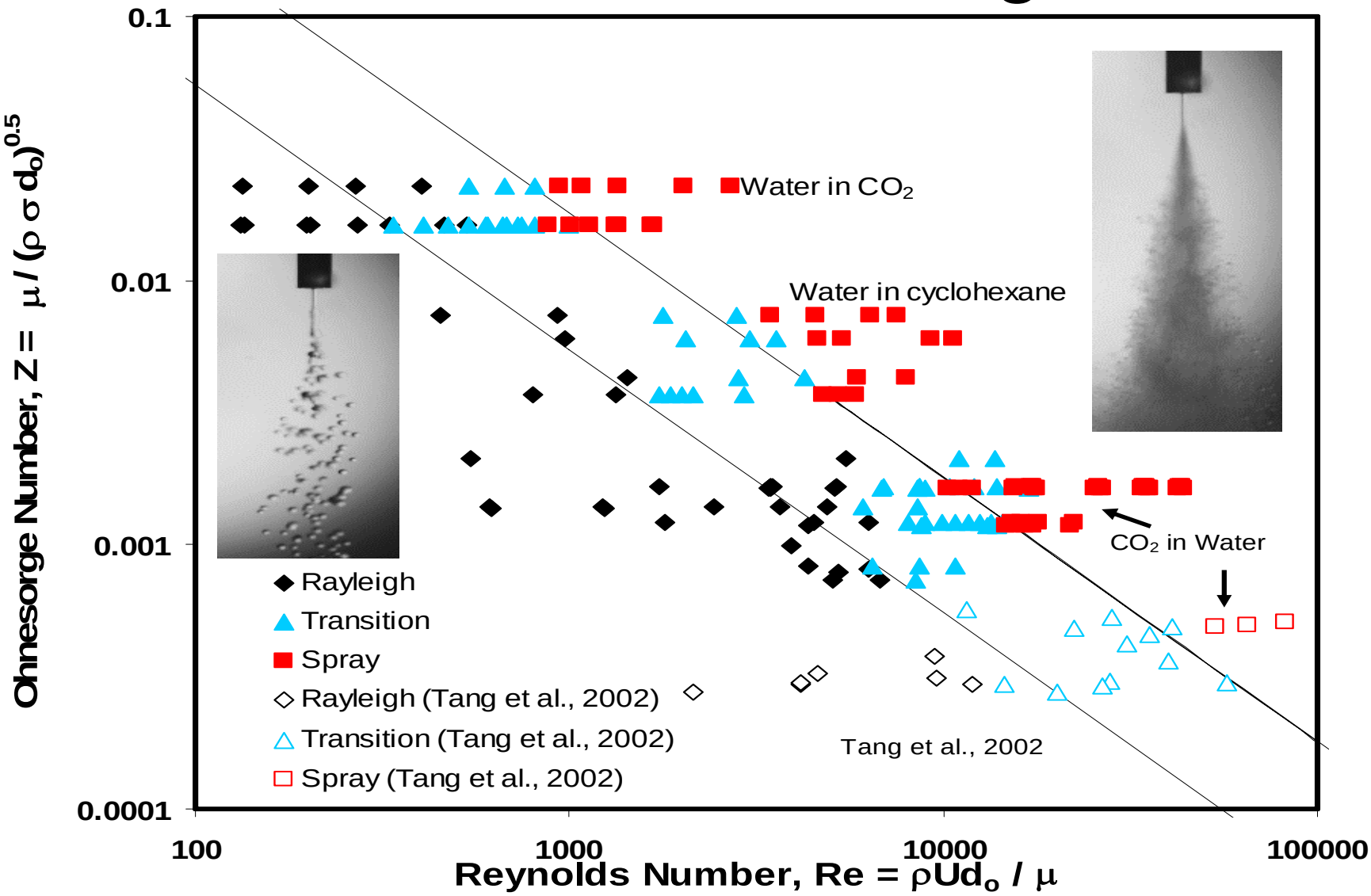
Scale-up CJHR Reactors



(a) Single-capillary, concentric injector
(b) Capillary-array injector

Reactor scaleup is the next step in employing CO_2 hydrate formation in ocean carbon sequestration.

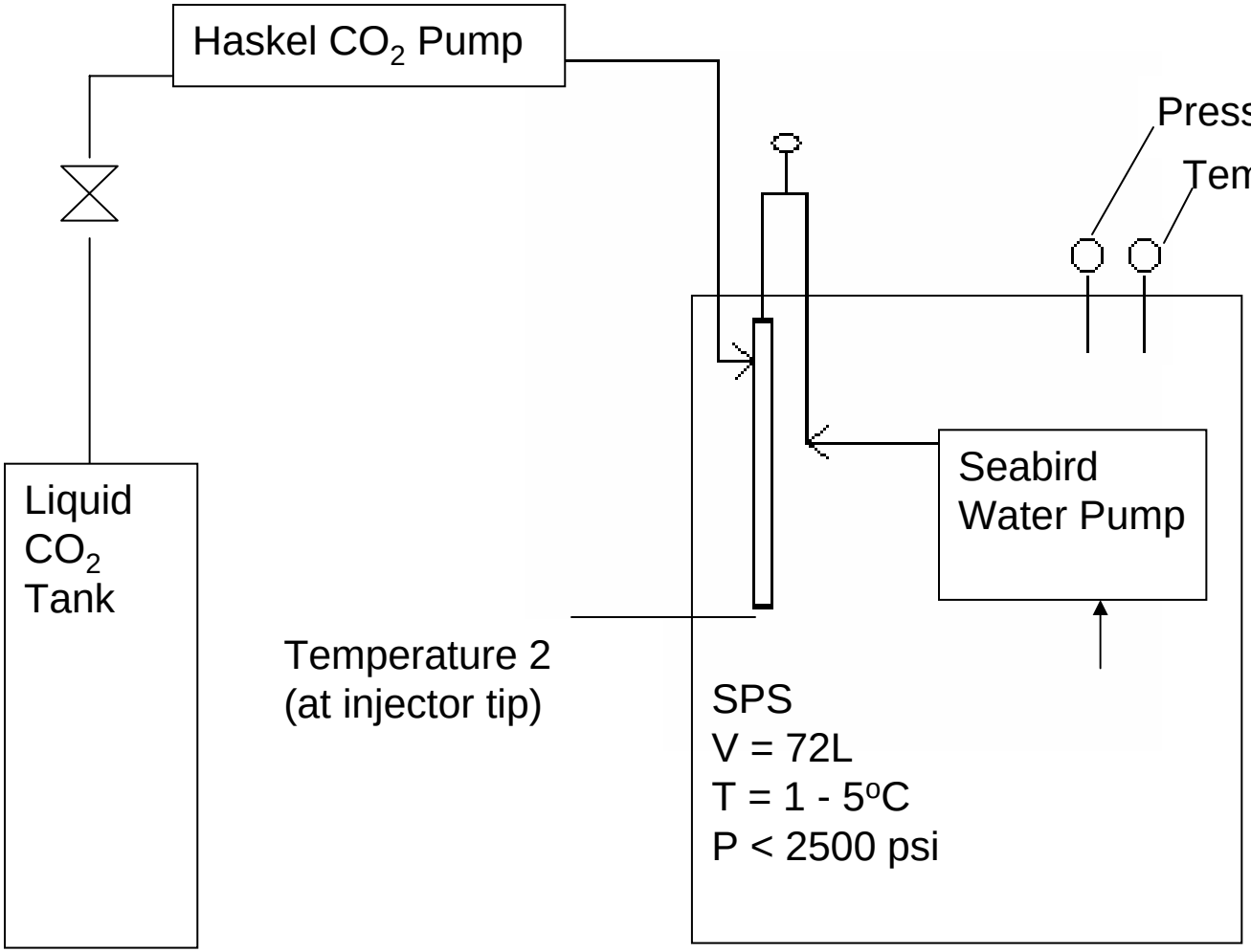
Jet Destabilization Regimes



Jet breakup regimes identified in the Ohnesorge vs. Reynolds number diagram.

Riestenberg et al., Amer. Mineralogist, 2004

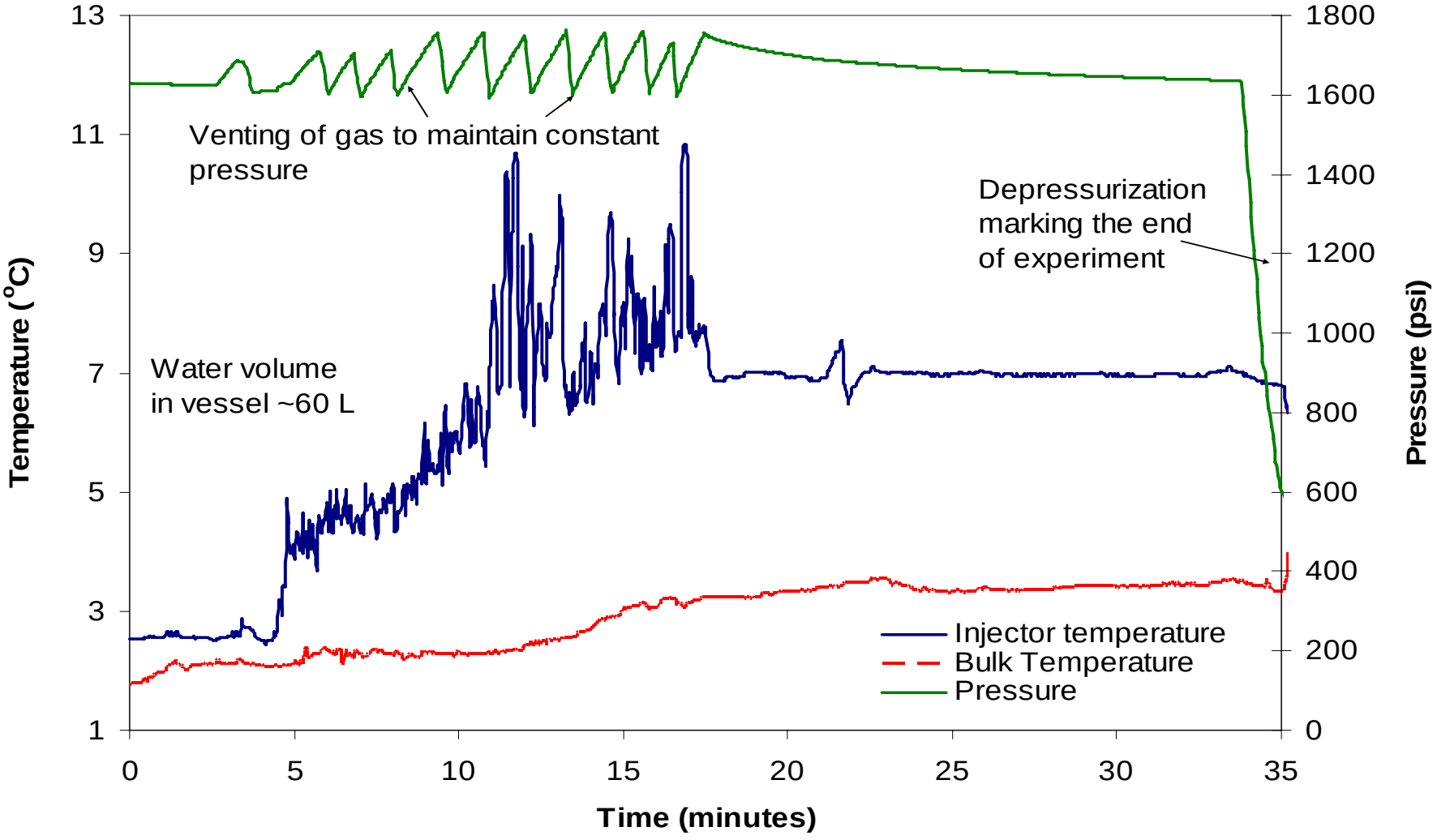
Experimental Setup for Scale-up Studies



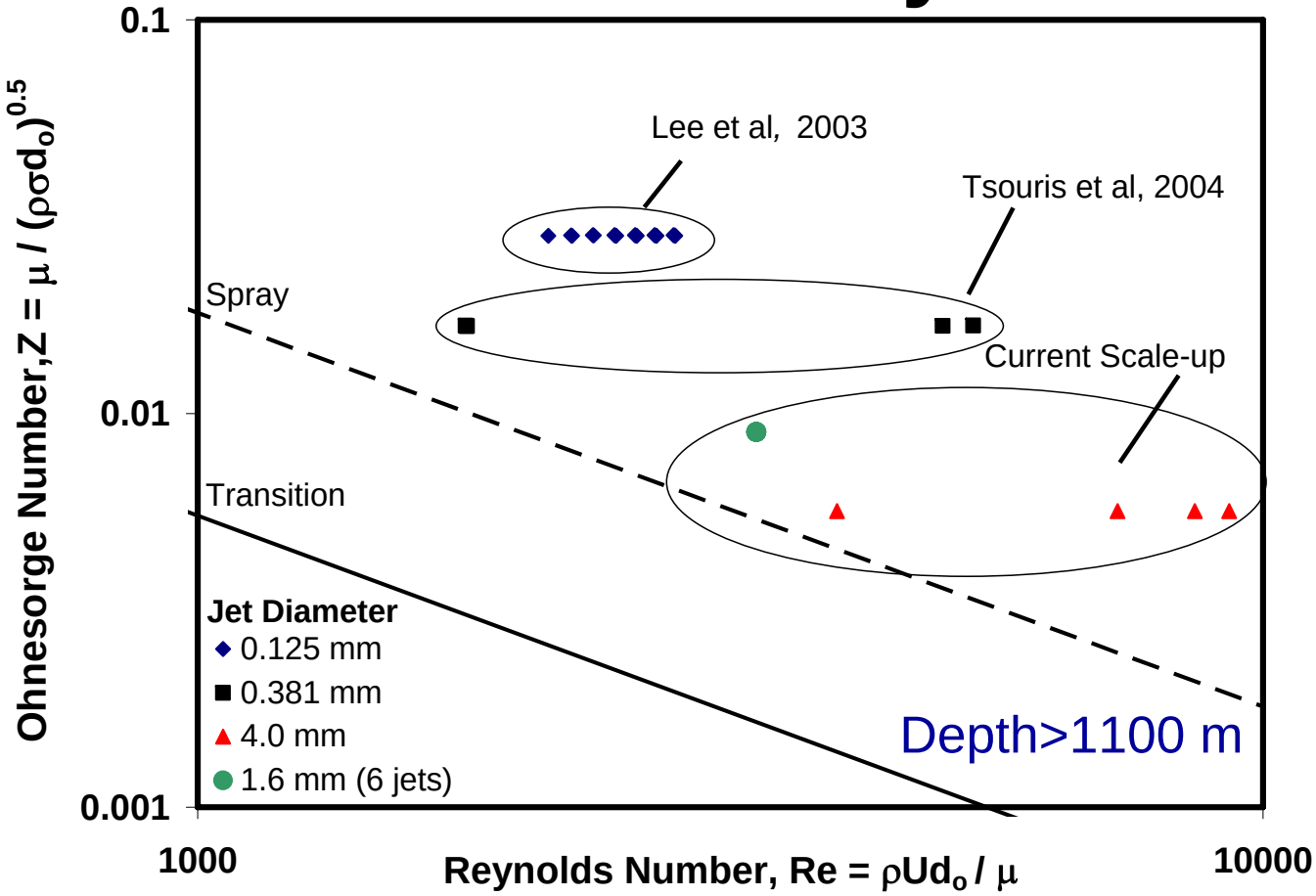
The experimental setup for the scale-up experiments included a submersible water pump operating at a high pressure and an externally mounted pulsed CO_2 pump.

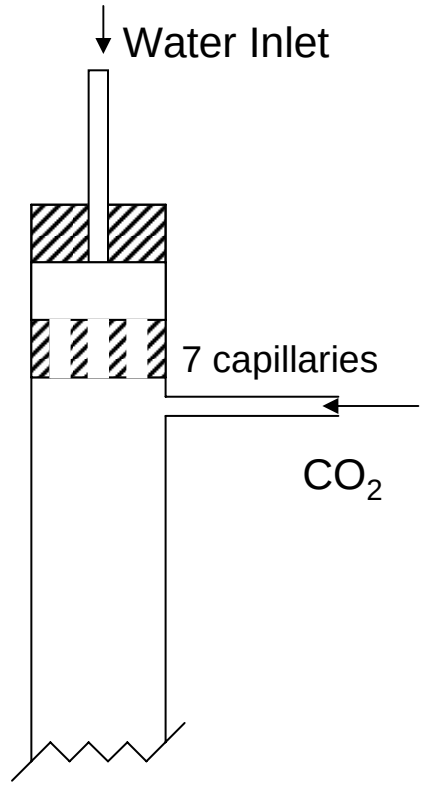
The CJHR Reactor Works in Different Modes (video clips)

Temperature-Pressure Histories for a Typical Experiment with the CJHR



Ohnesorge-Reynolds Diagram is Used to Select Geometry and Flowrates





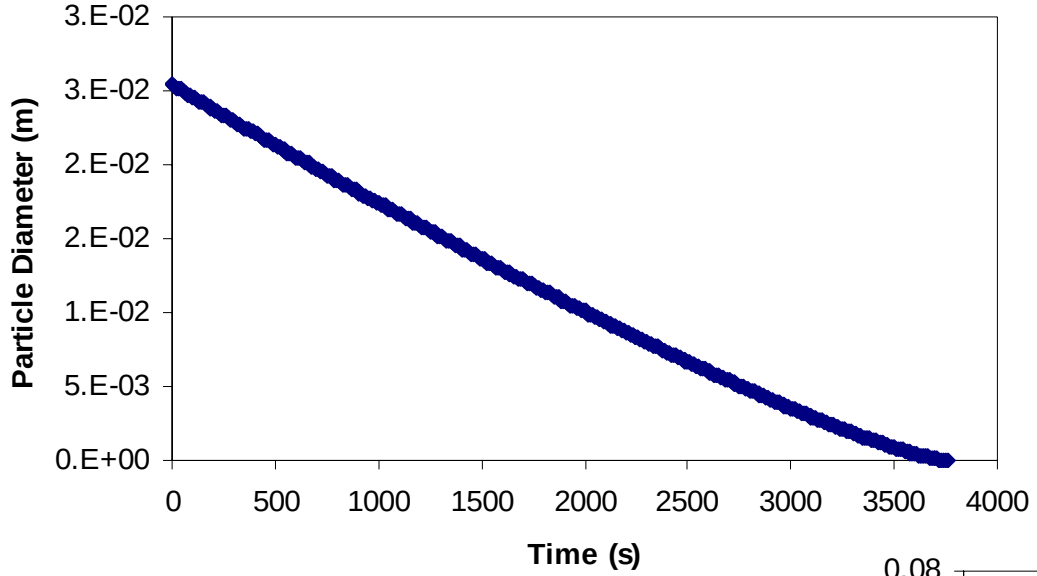
$$We = (\mathrm{Re} * Z)^2 = \frac{\rho_d u^2 d_o}{\sigma} \geq 1024$$

$$d_o \leq 0.032 \left(\frac{\rho_d Q_d^2}{\sigma} \right)^{1/3}$$

An average power plant emits 4.3 Mt CO_2/yr): ~ 740 capillary-array CJHR units with 8.9-mm internal diameter for each capillary are needed.

Tsouris et al., in preparation

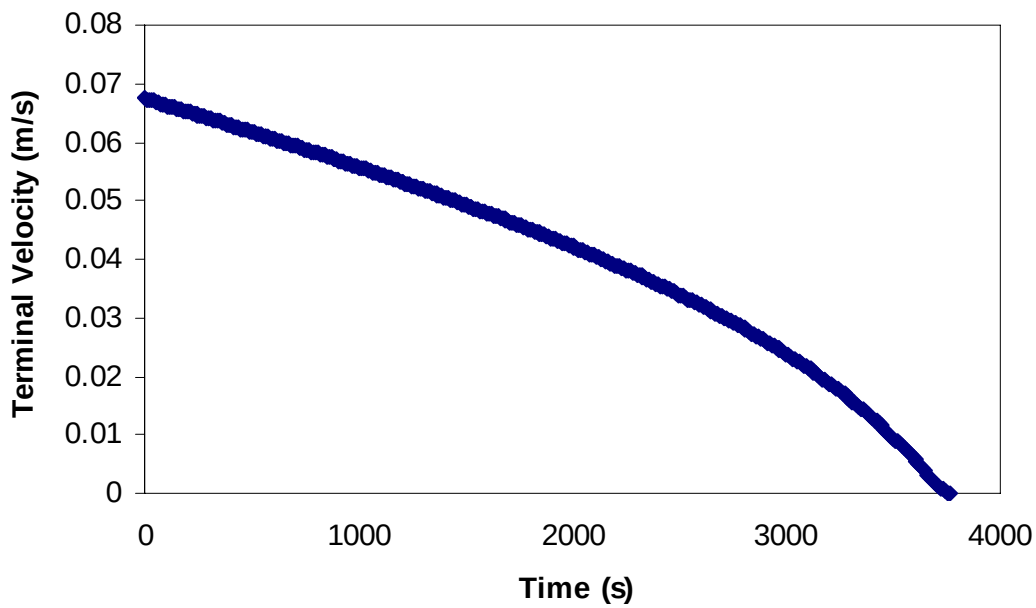
CO_2 Hydrate Dissolves as it Descends in Seawater



Mass-transfer modeling based on single particle

Additional effects occur in a plume, allowing the particles to descend for as much as 1000 m before dissolution:

- Solute density effect: Seawater density increases due to CO_2 dissolution
- Plume effect: Particles sink with plume velocity plus settling velocity



Riestenberg et al., ES&T, 2005

Summary and Conclusions

- **CO_2 hydrate formation and dissociation were studied in the laboratory (ORNL-SPS and NETL-HWTF) and in the field.**
- **A Continuous-Jet Hydrate Reactor was developed for the continuous formation of CO_2 hydrate from liquid CO_2 and surrounding seawater.**
- **Hydrate formation produced dense particles that could sink, carrying CO_2 to depths well below the injection point.**
- **A mass-transfer model coupled with the particle velocity and drag force was developed to predict the particle diameter and depth with time.**
- **Scaleup of the CJHR reactor was successful. The throughput was scaled-up by two orders of magnitude without loosing the important properties of the particles, i.e., density and cohesiveness.**

Acknowledgments

This work is supported by the Ocean Carbon Sequestration Program, Office of Biological and Environmental Research, U.S. Department of Energy under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.

<u>Collaborators</u>

Peter Brewer, Edward Peltzer, Peter Walz (MBARI)

Eric Adams, Aaron Chow (MIT)