Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

Section 3D: Advanced Capture

CO_2 Hydrate Formation in a Continuous Flow Reactor

- Engineering Test Module (ETM)

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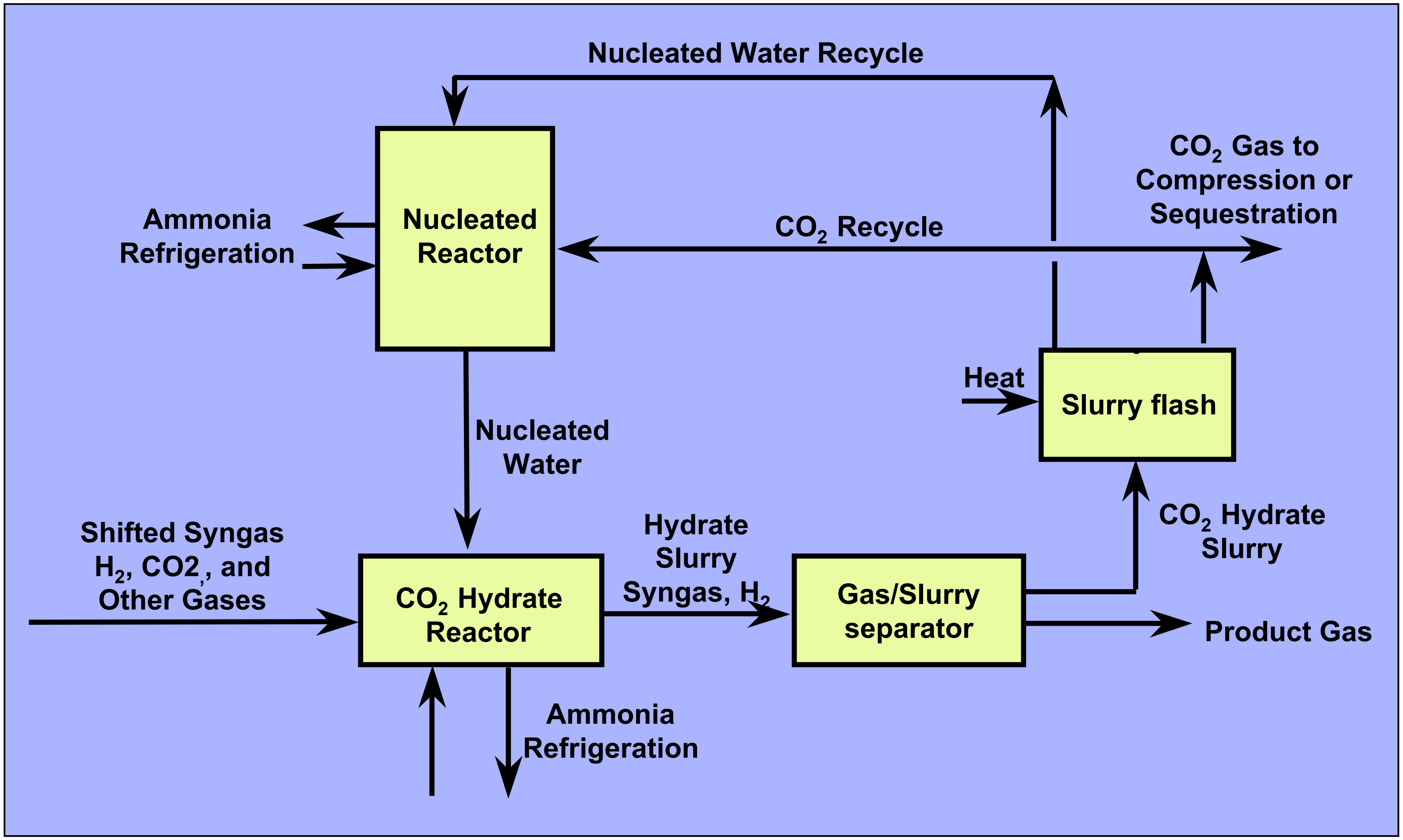
Hydrate Process for Gas Separation in IGCC Plant



"Fossil fuels currently supply over 85% of the energy in the United State of America. The combustion of these fossil fuels is responsible for ~ 90% of the greenhouse gas (GHG) emissions in the U.S. ***Use of these fuels, national and world- wide, is expected to increase significantly in the 21st century".***

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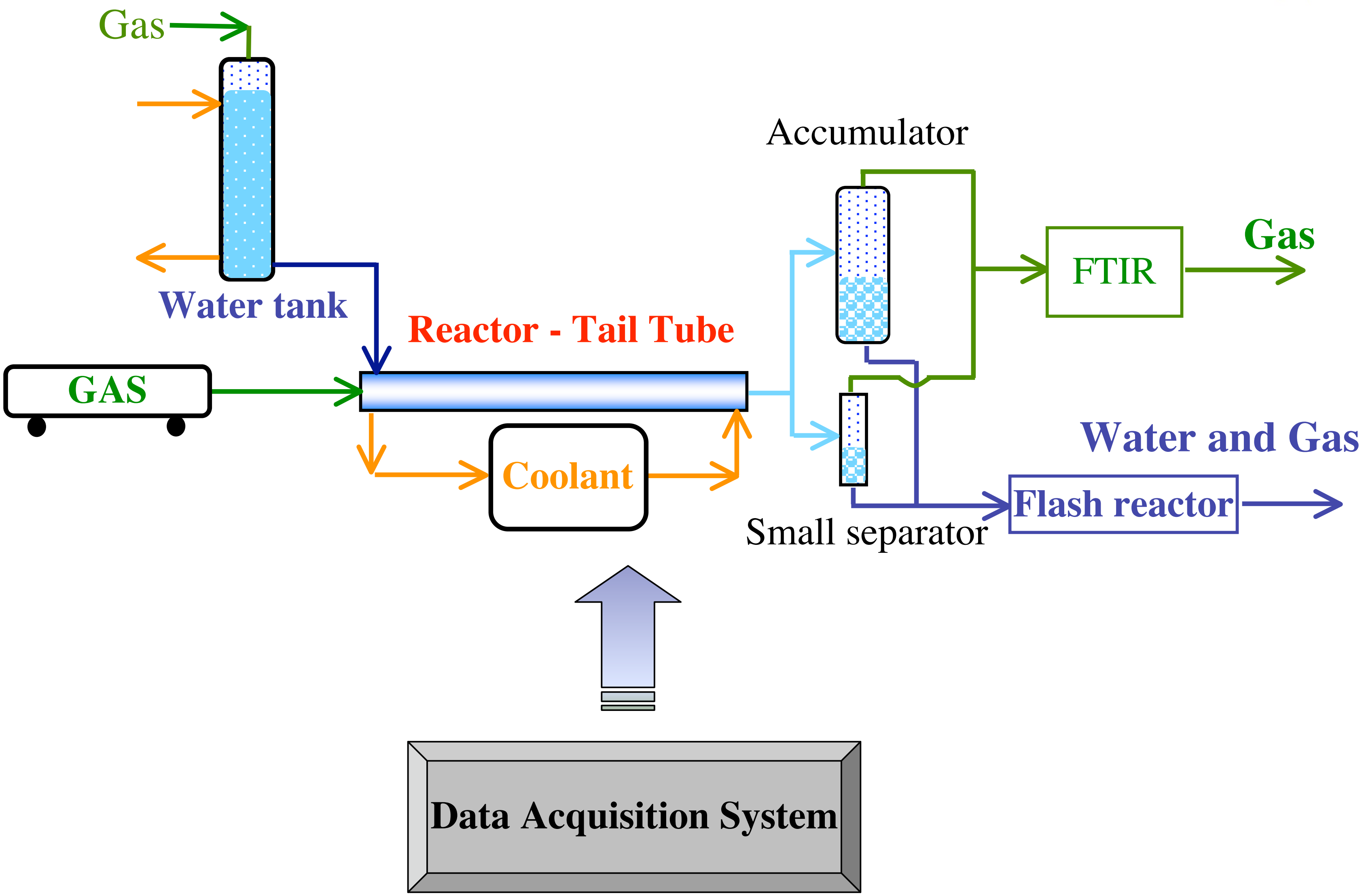
Objectives of the Engineering Test Module (ETM)

- Conduct experiments under the flow conditions closer to industrial operation conditions (fluid velocity > 10 ft/sec)
- Investigate the effect of operation parameters on the CO_2 conversion rate in a continuous flow reactor
- Develop theoretical models to simulate the hydrodynamic and kinetic mechanisms of CO_2 hydrate formation in dynamic conditions and for scale-up design
- Demonstrate the feasibility of using clathrate technology to remove CO_2 from syn-gas on an industrial scale

Conceptual ETM Flowchart



Engineering Test Module (ETM) in LANL

Gas delivery system

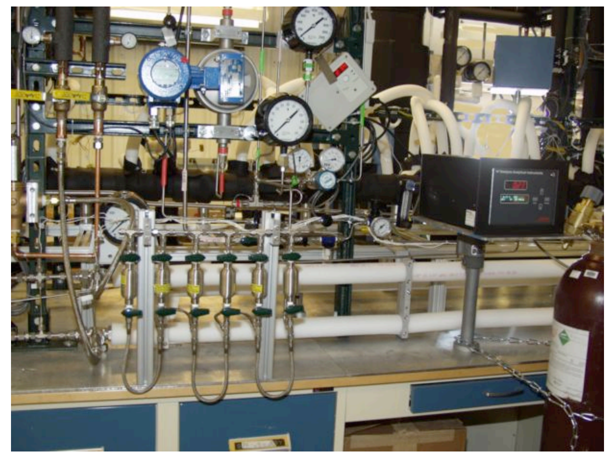
Raw and conditional water delivery systems

Continuous Flow Reactor

Accumulators

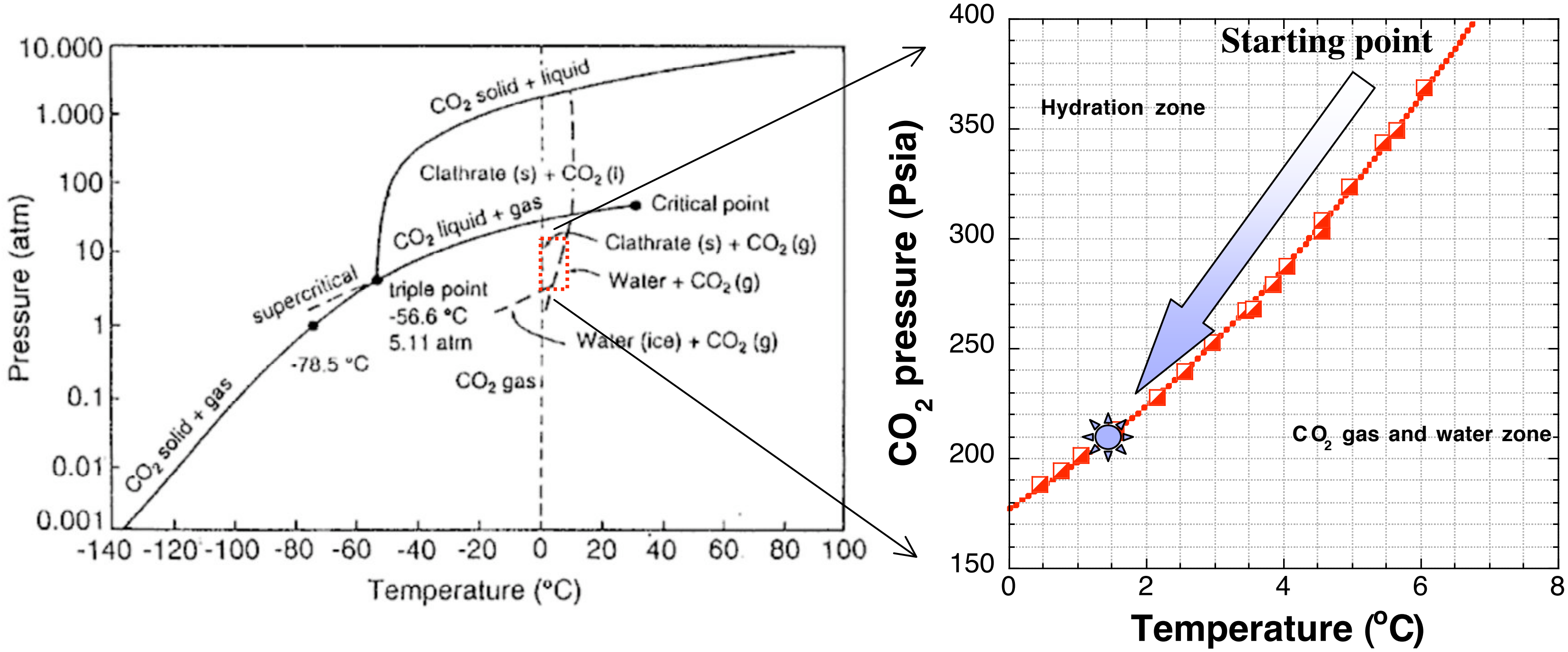
Data acquisition system

Flow control and instrumentation systems



Gas sample station and analyzer systems

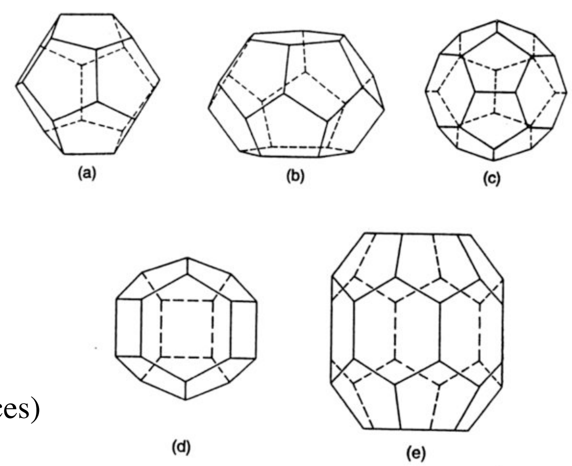
Thermodynamics of the CO_2 - Water System



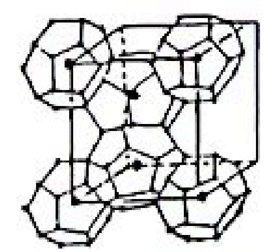
GAS HYDRATE CAVITIES:

a. pentagonal dodecahedron (5^{12})
b. tetrakaidecahedron ($5^{12}6^{2}$)
c. hexakaidecahedron ($5^{12}6^{4}$)
d. Irreg. Dodecahedron ($4^{3}5^{6}6^{3}$)
e. icosaherdon ($5^{12}6^{8}$)

Polyhedron Notation:
n^m = m faces with n edge
(5^{12} = polygon with 12 pentagonal faces)



Structure I



46 Water Molecules

C. N. MURRAY, *L. VISINTINI G. BIDOGLIO, B. HENRY,*
Paper presented to the International Conference "Greenhouse Gases: Mitigation Options"
22-25 August 1995, London, UK.

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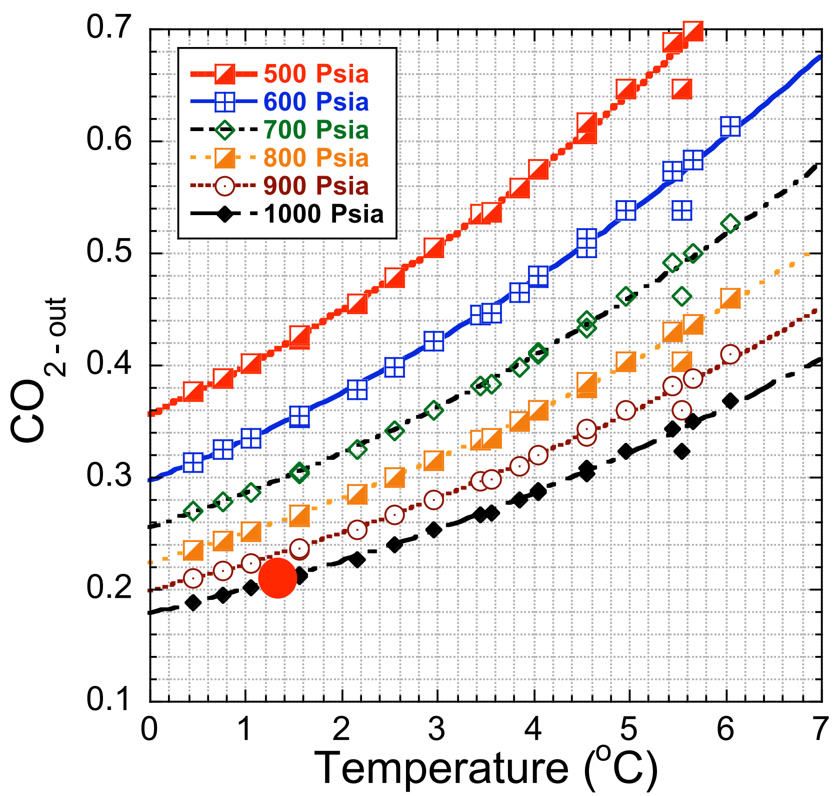
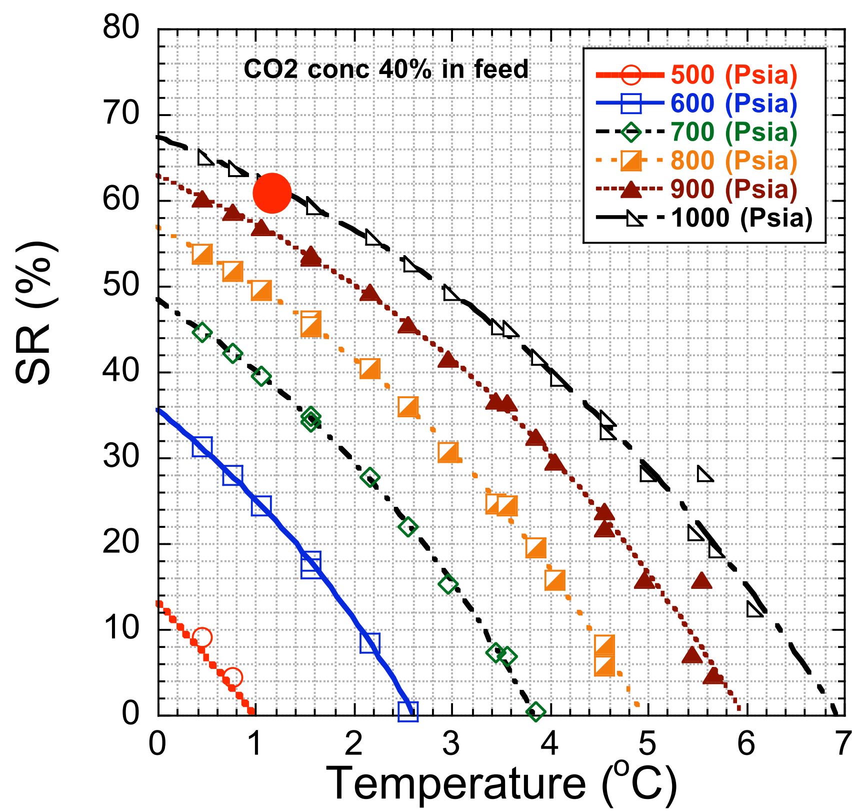
Effect of Total Pressure on CO_2 Conc. in off Gas

(at CO_2 - hydrate equilibrium state)





$$SR = 1 - \frac{C_{CO2-out}/(1 - C_{CO2-out})}{C_{CO2-in}/(1 - C_{CO2-in})}$$

Where:
SR: Separation ratio
$C_{CO2\text{-}out}$: CO_2 molar fraction in off gas
$C_{CO2\text{-}in}$: CO_2 molar fraction in feed gas

Equilibrium at 1000 Psia and 1.33 °C
The Separation ratio is 61%.
CO_2 concentration in off gas is 21%.

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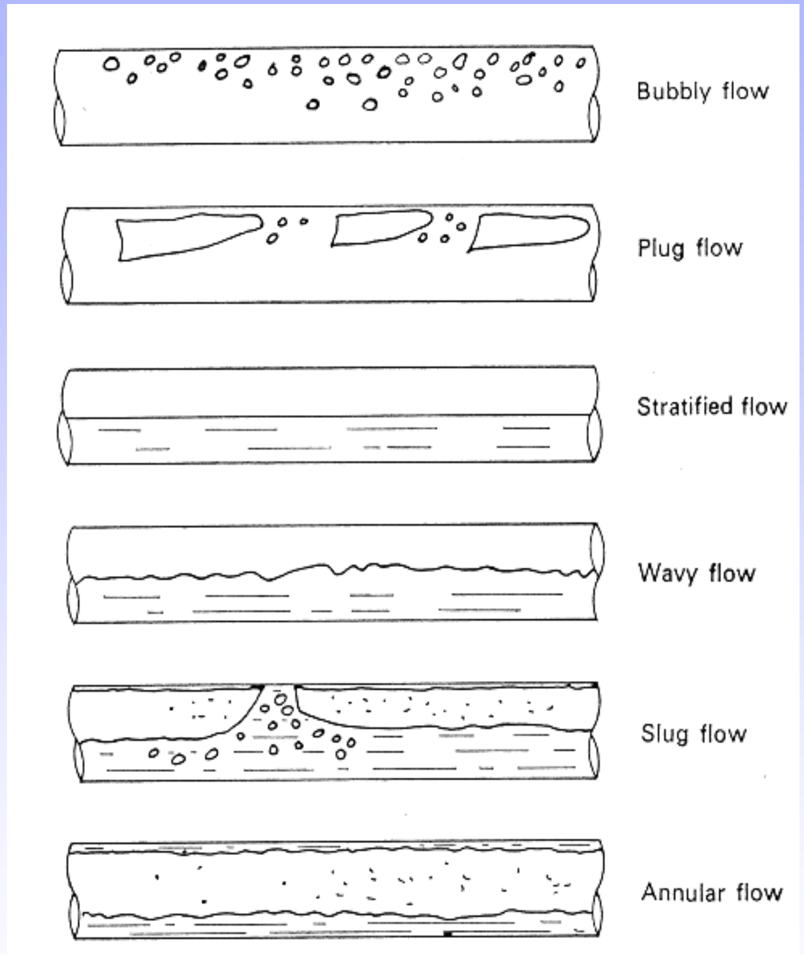
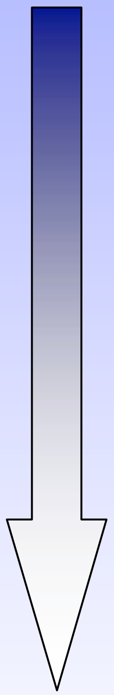
Effect of Flow Pattern on Hydrate Formation in ETM

- Flow pattern depends on velocities, liquid/gas molar ratios, and physical properties of components.
- Flow pattern impacts heat transfer efficiency, and thus impacts on reaction rate.
- Flow pattern affects interfacial area between gas and liquid phases.
- Flow regime affects ease of separation of gas from slurry/liquid phase.



Cited from "The flow of complex mixture in pipes" G. W. Govier

Water/CO_2 MR > 26



Water/CO_2 MR < 10

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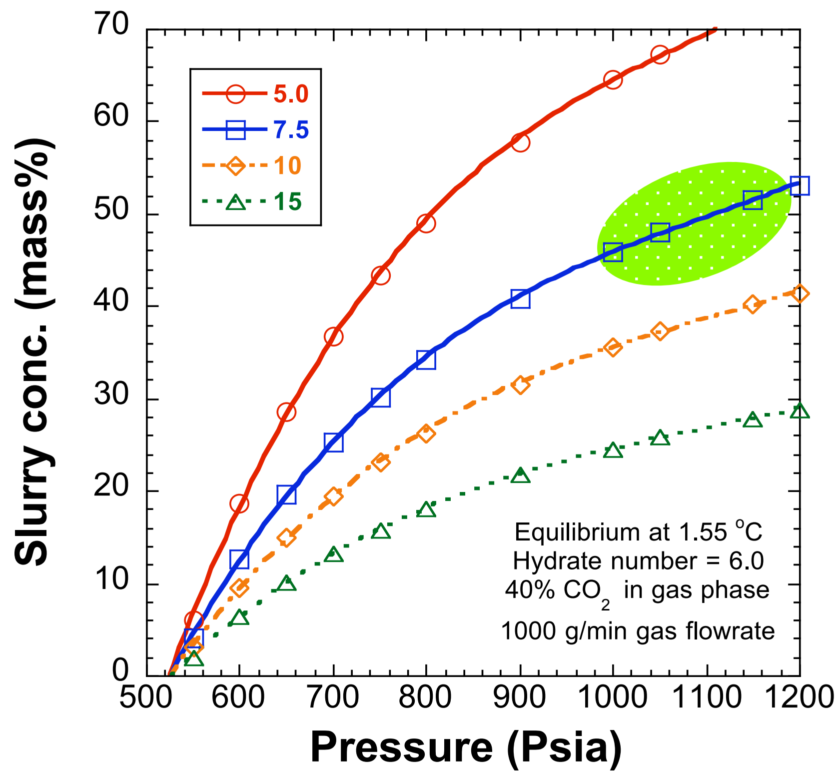
Effect of Water/CO_2 Molar Ratio on Slurry Concentration

$$nH_2O_{(L)} + CO_{2(G)} \xrightarrow[P,T]{\Delta H} CO_2 \bullet H_2O_{m(S)}$$

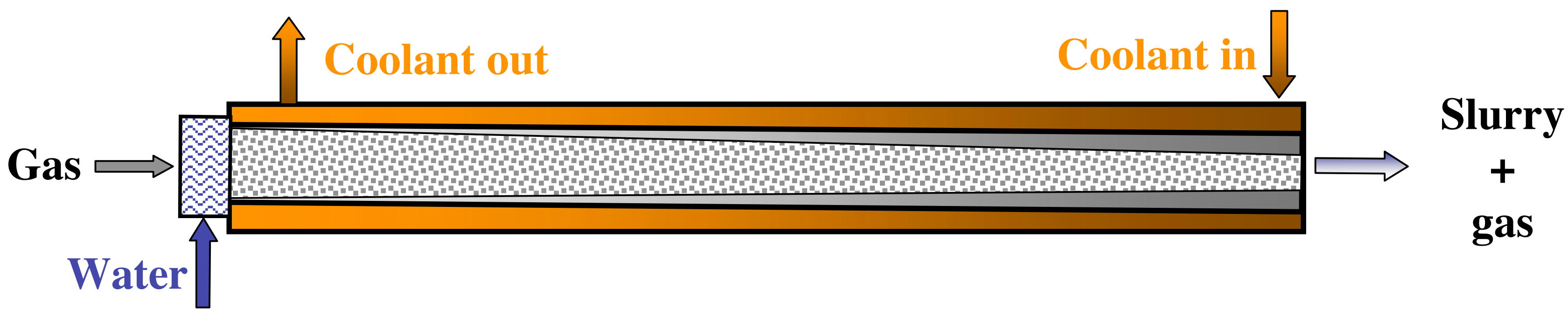
$$m \approx 5.8 - 6.4$$

$$\Delta H = -60\ KJ/mol$$



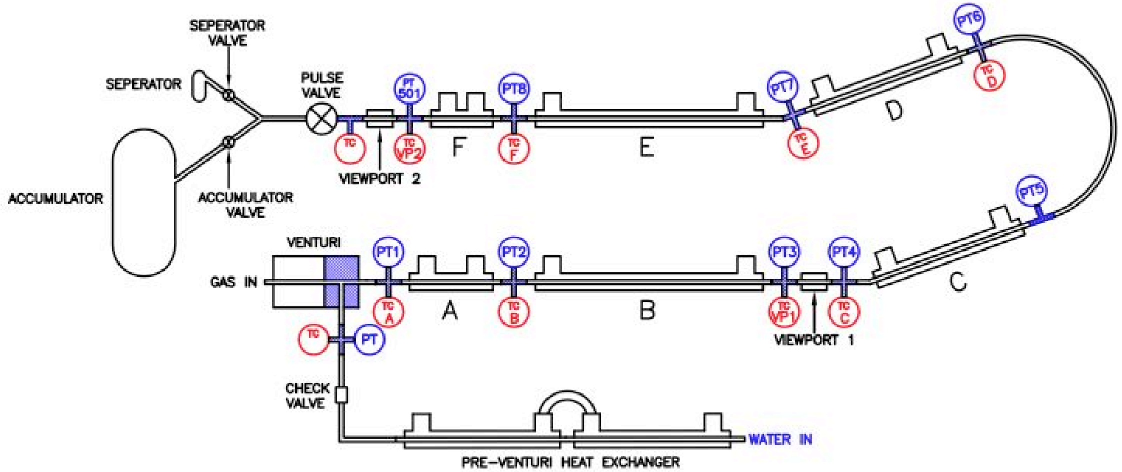
Challenges

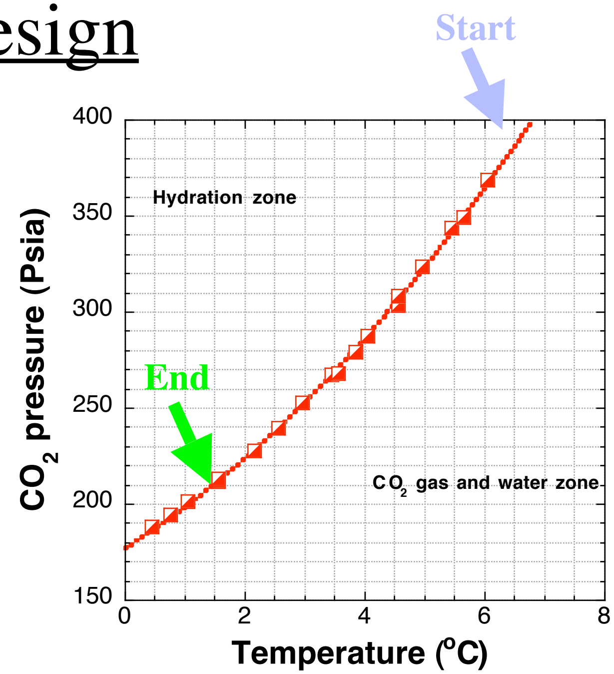
- ***Multiphase flow (G-L-S)***
- ***Large heat generation***
- ***High gas volume fraction***
- ***High slurry concentration***



Experimental Design

Flowchart of the CFR





Conditions:

- *Ar as a surrogate gas for H_2*
- *Pressure: 600 - 1300 Psia*
- *Temperature: < 10 °C*
- *Water/CO_2 molar ratio: < 10*
- *CO_2 molar fraction: < 60%*

Expected Results:

- *Heat removal from the reactor*
- *Hydrate formation rate*
- *CO_2 concentration change*
- *Slurry concentration change*
  - ✓ *Heat Transfer*
  - ✓ *Mass transfer*
- *Fluid velocity impact*
  - ✓ *Heat Transfer*
  - ✓ *Mass transfer*

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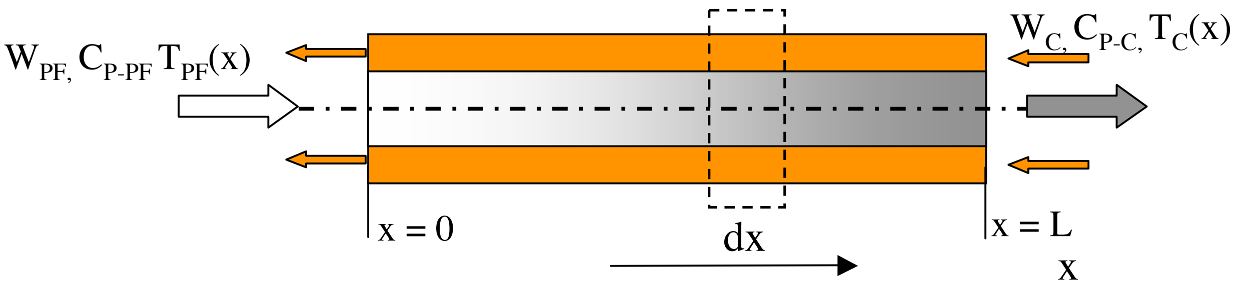
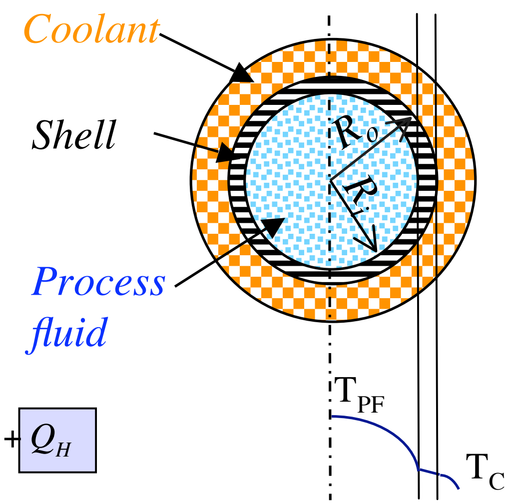
Heat Balance between Process Fluid and Coolant





$$\text{For Process Fluid:} \quad W_{PF} \bullet C_{P-PF} \bullet \frac{dT_{PF}(x)}{dx} = -U * \pi D_i * (T_{PF}(x) - T_C(x)) + \boxed{Q_H}$$

$$\text{For Coolant Fluid:} \quad W_C \bullet C_{P-C} \bullet \frac{dT_C(x)}{dx} = U * \pi D_i * (T_{PF}(x) - T_C(x))$$

$$if\ Q_{\mathrm{H}} = 0$$

Over - all heat transfer coefficient :

$$U = -\frac{1}{L} * \ln\left(\frac{T_{PF}(L) - T_C(L)}{T_{PF}(0) - T_C(0)}\right) * \frac{W_{PF} * C_{P-PF} * W_C * C_{P-C}}{W_{PF} * C_{P-PF} + W_C * C_{P-C}} * \frac{1}{\pi D_i}$$

Nomenclature:

W = Mass flowrate of mixture (g/sec),
C_p = *Heat capacity (J/g-K),*
T = Average temperature (°C),
D_i = *Inside diameter of tail tube (cm),*
Q_H = *Hydrate formation heat per unit length (J/cm),*
U = Over all heat transfer coeff. (J/cm²-sec-K),
L = Total length of the tail tube (cm),
$_{C,\ PF}$ = *Subscriptions for coolant and process fluid, respectively.*

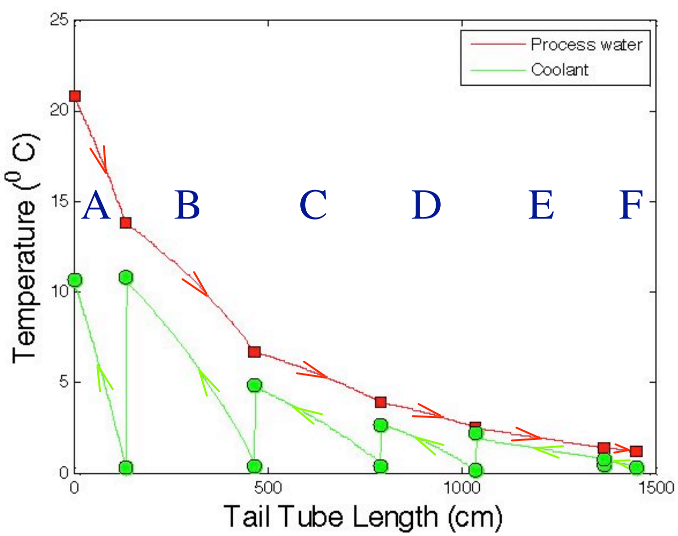
Temperature Profiles

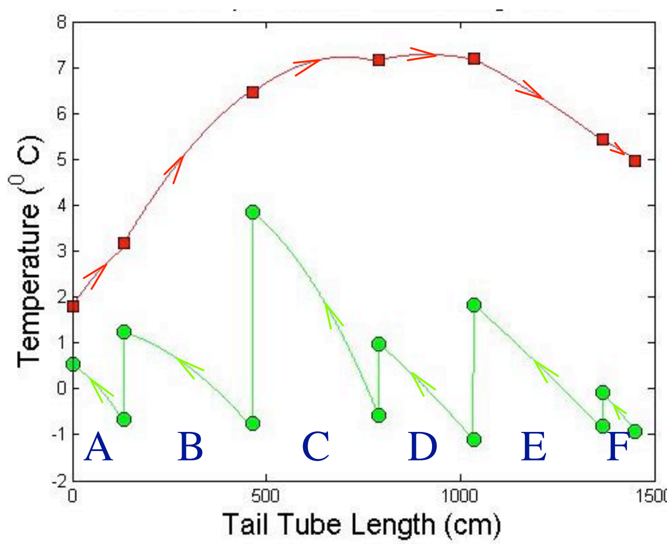
- N_2 and water runs under the flow conditions similar to hydrate production conditions
- Not reaction heat generated

  $Q_H = 0.$

- Hydrate production runs
- Exothermal reaction

  $Q_H > 0$





$$\text{For Process Fluid:} \quad W_{PF} \bullet C_{P-PF} \bullet \frac{dT_{PF}(x)}{dx} = -U * \pi D_i * (T_{PF}(x) - T_C(x)) + Q_H$$

$$\text{For Coolant Fluid:} \quad W_C \bullet C_{P-C} \bullet \frac{dT_C(x)}{dx} = U * \pi D_i * (T_{PF}(x) - T_C(x))$$

Wilson line technique:

$$\frac{1}{U} = K_1 + K_2 * V_C^{-0.33}$$

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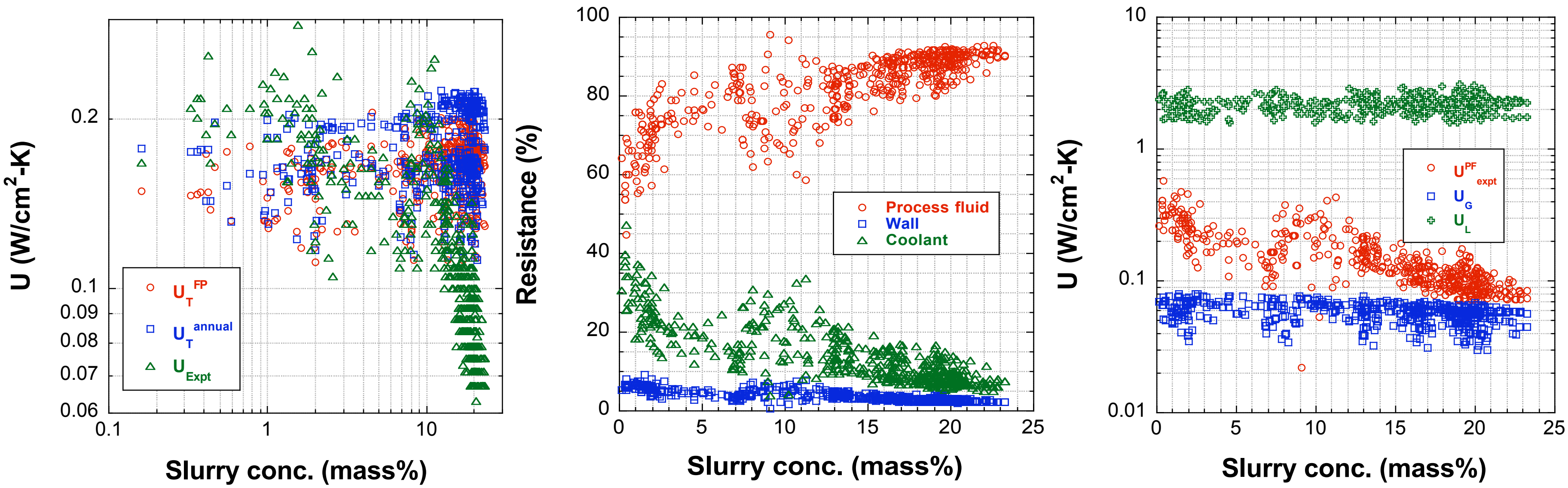
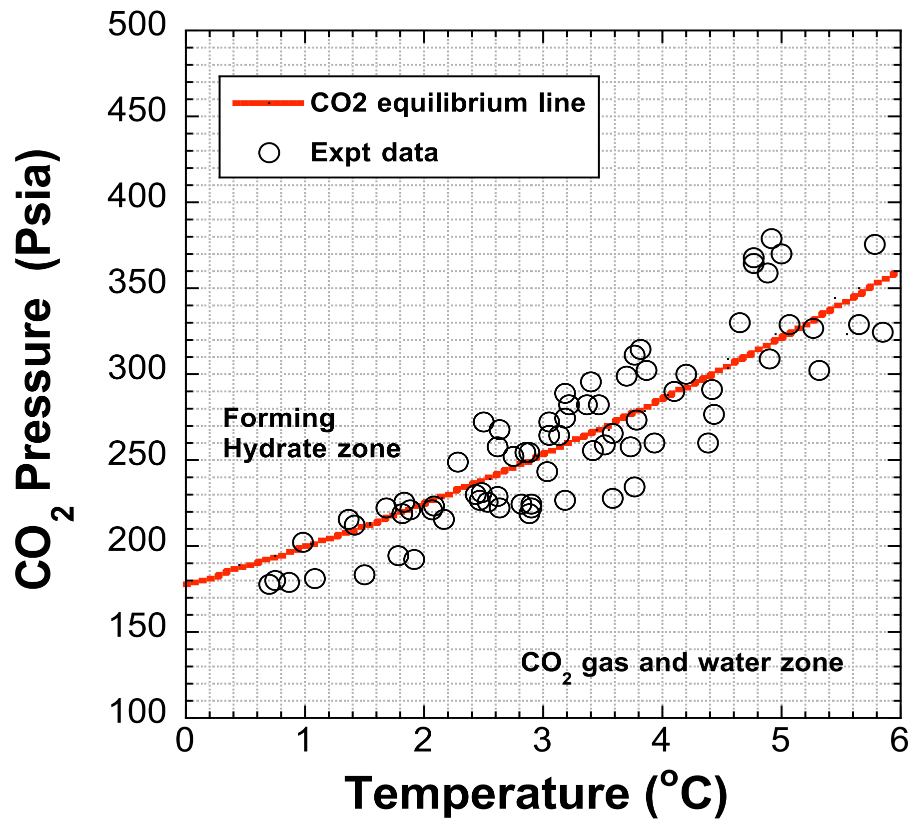
Heat Transfer Coefficients in Hydrate Formation



- ➢ Both empirical correlations are valid when slurry conc. < 10 mass%
- ➢ Overall U significantly decreases when slurry conc. > 10 mass%
- ➢ Major heat resistance comes from the process fluid side
- ➢ Gas phase dominates the heat transfer on the process fluid side when slurry conc. > 15 mass%

Reaching Thermodynamic Equilibrium



- Reach thermodynamic equilibrium at different temperatures!
- Longer tail tube length is needed to reach equilibrium in one stage at 1.33 °C.

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Conclusions

- Demonstrated CO_2 hydrate reaction is a fast reaction
  - induction time less than one second
- Can reach thermodynamic equilibrium at different temperatures
- Conducted more than 100 steady-state experiments
- Established a reliable engineering database for scale-up design
- Proved the high fluid velocity is critical for effective heat transfer and gas/liquid mixing
  - Interfacial reaction
  - Operational stability
- Believe CO_2 hydrate is a feasible technology to remove CO_2 from IGCC plant

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Thank You!