Controlling Hydrate Formation in Production Lines

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Jornadas em Escoamentos Multifásicos

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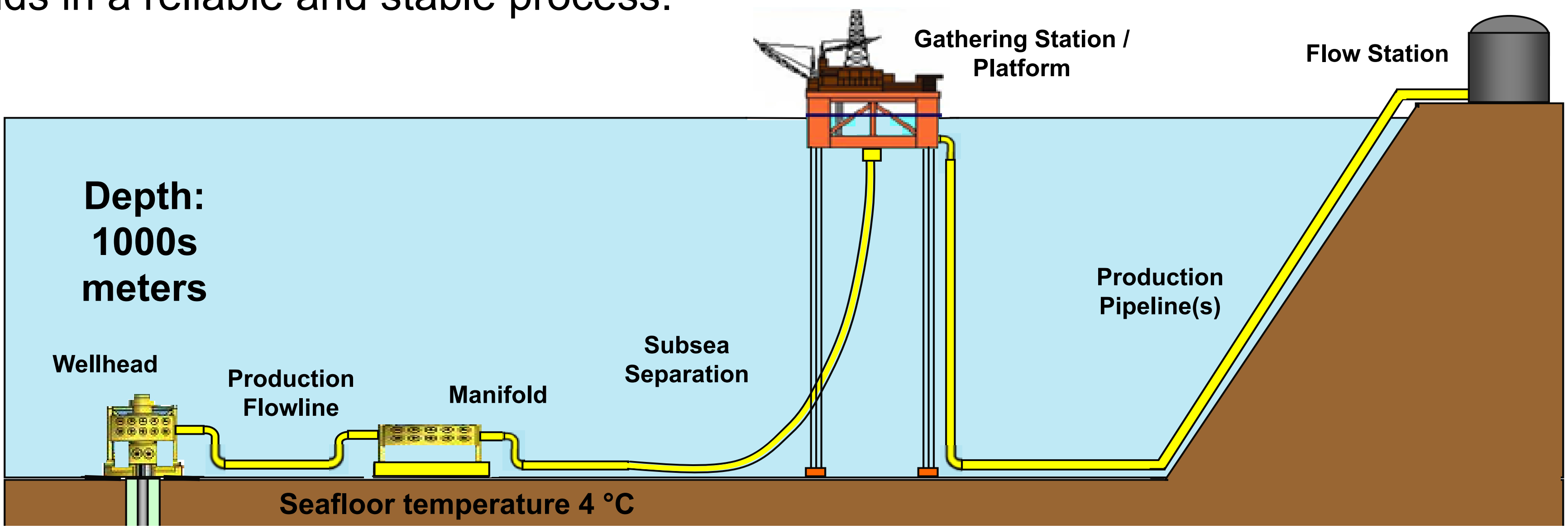
Hydrocarbon Production System

Flow Assurance*: Term used to describe the design, engineering, and management for transport of multiphase fluids in a reliable and stable process.

Separation of oil/gas/water



Produce oil/gas/water

Pipeline: 10s km
Oil: 6-8 inch
Gas: 10+ inch

*Coined by Petrobras in the early 1990s as "Garantia de Escoamento"

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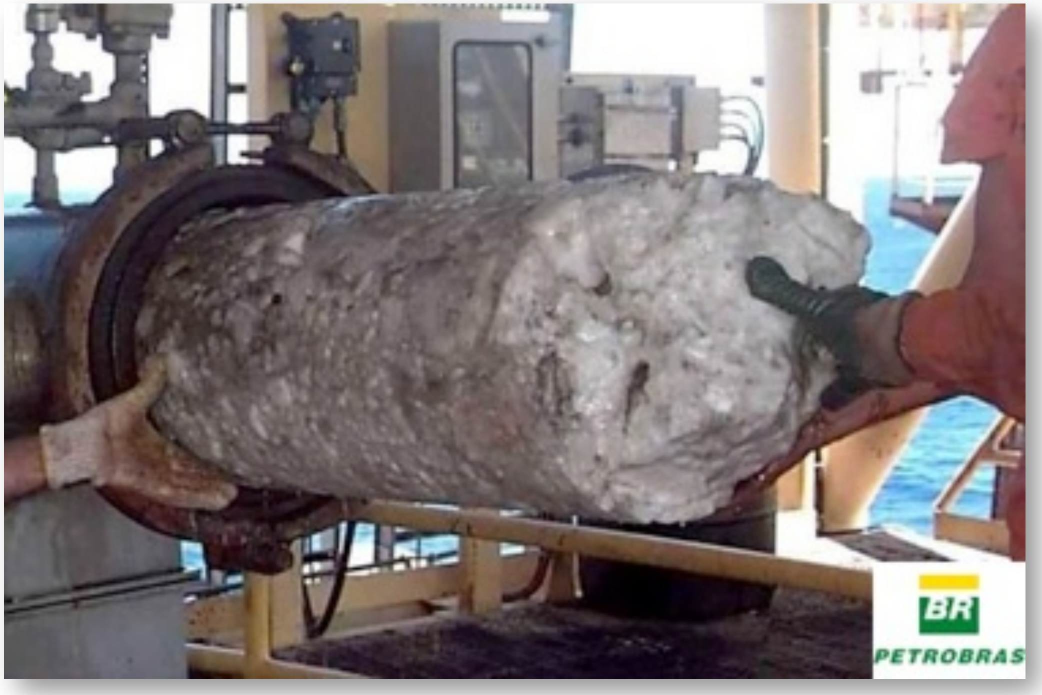
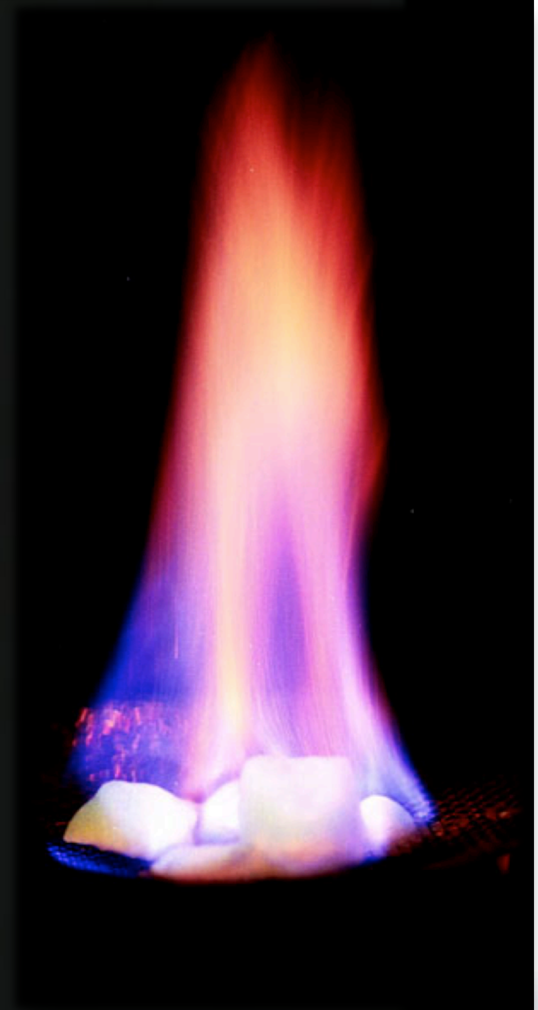
Hydrates in Flow Assurance

- **Hydrate formation in oil/gas flow lines**
- **#1 problem in flow assurance (more severe than wax, asphaltene, corrosion)**
- **Costly to prevent ($100sM per year)**
- **Costly to remove (lost production)**
- **Safety concern (pressure buildup)**

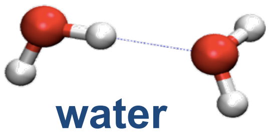
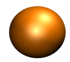


Hydrate plug removed from oil pipeline

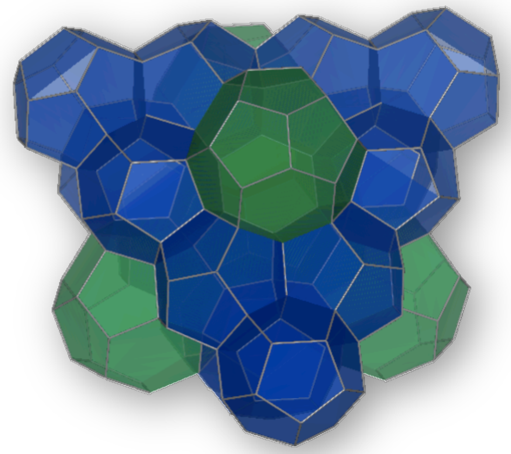
Burning Hydrate



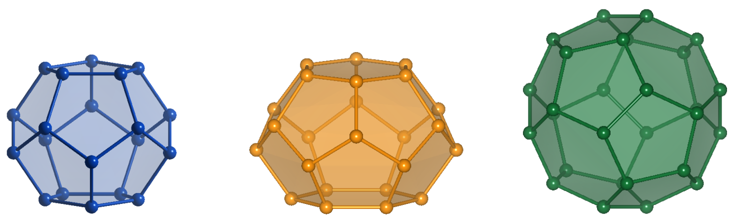
Hydrates Fundamentals


water
+ gas

+ High *P*
Low *T*

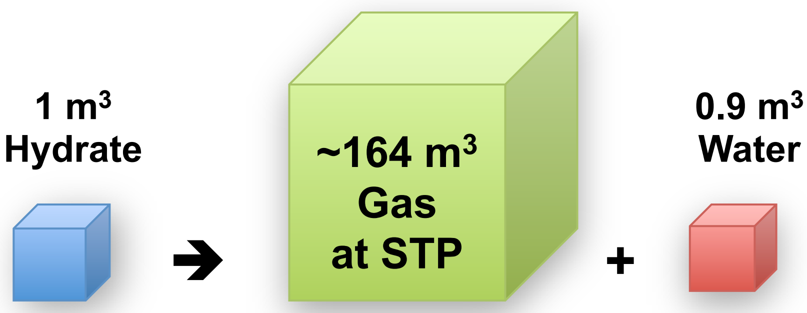
crystal structure



Burning hydrate



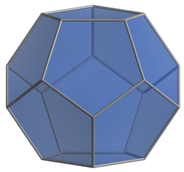
water cages



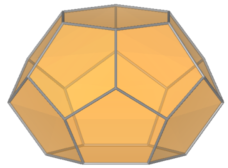
Typical hydrate forming gases:

- Methane
- Ethane
- Propane
- Carbon Dioxide
- Nitrogen
- Hydrogen
- Xenon
- Acetone

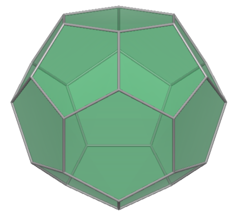
Hydrate Structures and Building Blocks



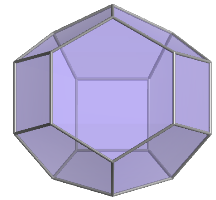
5^{12}
($20\ H_2O$)



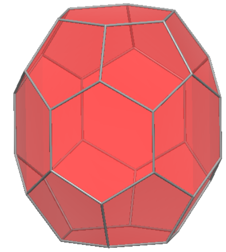
$5^{12}6^{2}$
($24\ H_2O$)



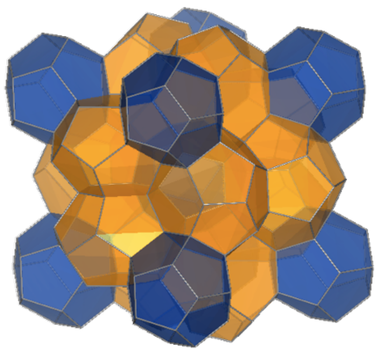
$5^{12}6^{4}$
($28\ H_2O$)



$4^{3}5^{6}6^{3}$
($20\ H_2O$)

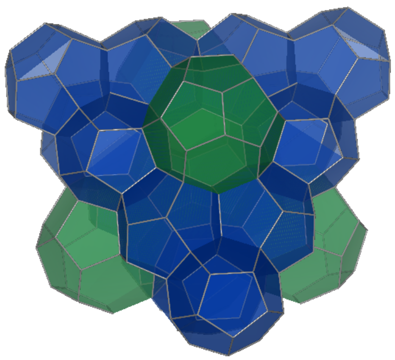


$5^{12}6^{8}$
($36\ H_2O$)



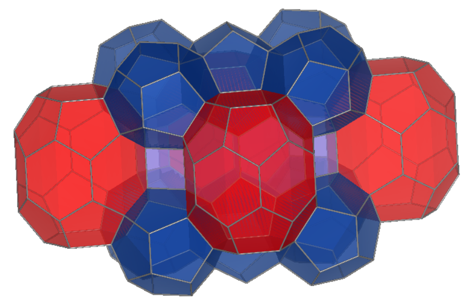
Structure I

$2(5^{12}) + 6(5^{12}6^{2}) / 46\ H_2O$



Structure II

$16(5^{12}) + 8(5^{12}6^{4}) / 136\ H_2O$



Structure H

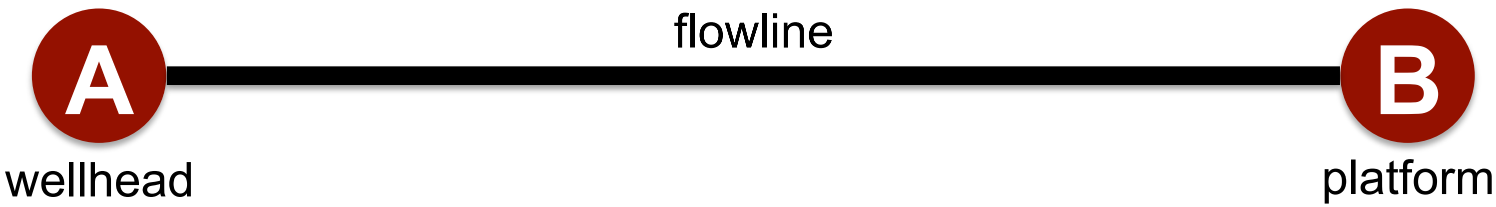
$3(5^{12}) + 2(4^{3}5^{6}6^{3}) + 1(5^{12}6^{8}) / 136\ H_2O$

- **At least 82% water**
- **One small molecules per cage**
- **Inclusion, crystalline compounds**
- **Non-stoichiometric compounds**

Depth and Breadth of Hydrate Research

lab scale
multiphase flow chemical inhibition
particle jamming/bedding
flowloop interfacial/surface science
heat transfer
mass transfer kinetics
simulations thermodynamics
aggregation modeling
nucleation phenomemon
rheology theory
emulsification
experiments

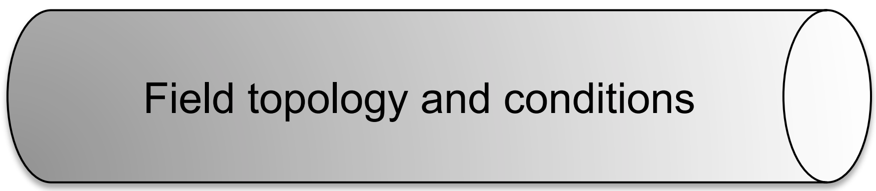
Hydrates in Flow Assurance



SPECIFIED

Fluid composition and properties
Phase fractions
Thermo conditions
Flow rate

CONSTRAINTS



NEED TO KNOW

Flow regime
Temperature/Pressure profile
Phases distribution, entrainment, emulsification
Hydrate avoidance/management
Hydrate amount, distribution
Hydrate remediation

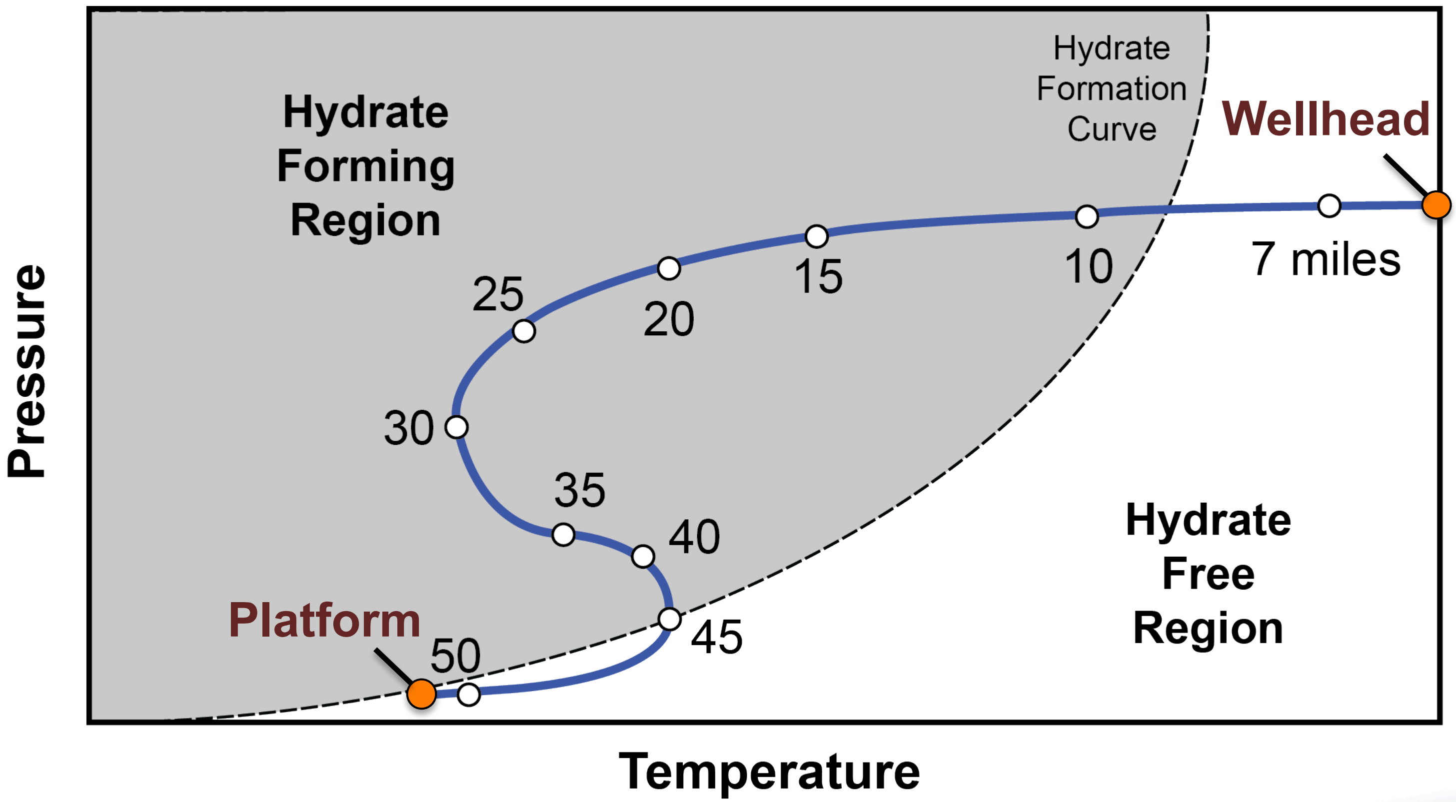
DESIRED

Producing fluids

Maximize flow
Minimize ΔP

Hydrates in Flow Assurance

Are hydrates a problem?



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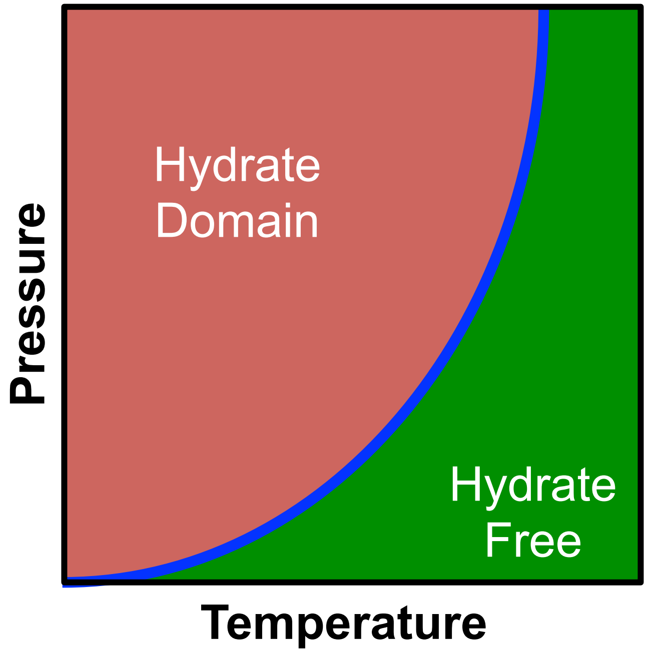
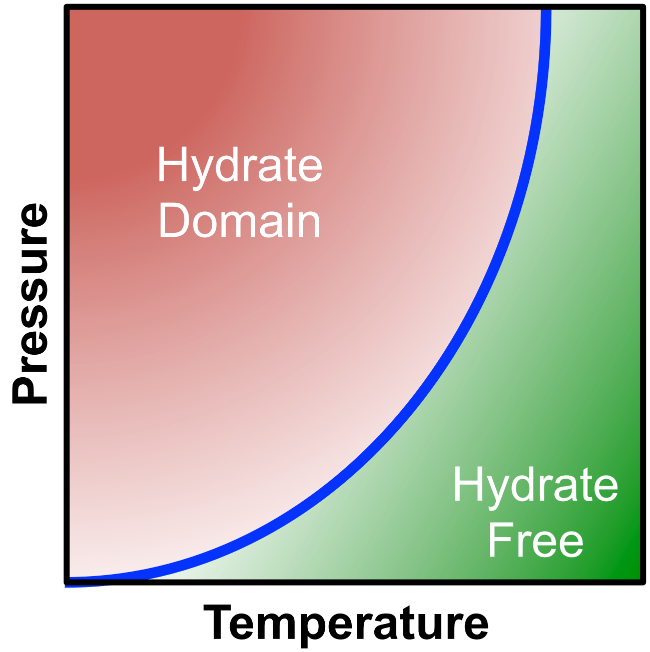
Hydrate Control Approaches

Hydrate Avoidance
(no entry in hydrate domain)



Hydrate Management
(operate with *risk* in hydrate domain)



Hydrate Management Strategies

- **Thermal**
  - Insulation
  - DEH
  - Bundles
  - Heat tracing
- **Chemical**
  - MeOH/EtOH
  - Glycols
  - LDHI (AA, KHI)
  - Salts
- **Hydraulic**
  - Fluid displacement
  - Gas sweep
  - Depressuriz-ation
  - Compression
  - Dense phase
- **Process**
  - Gas dehydration
  - Water cut reduction
- **No Control**
  - Operation within hydrate domain
  - Natural hydrate transport-ability
  - Natural kinetic inhibition

Modified from K. Kinnari (Statoil)

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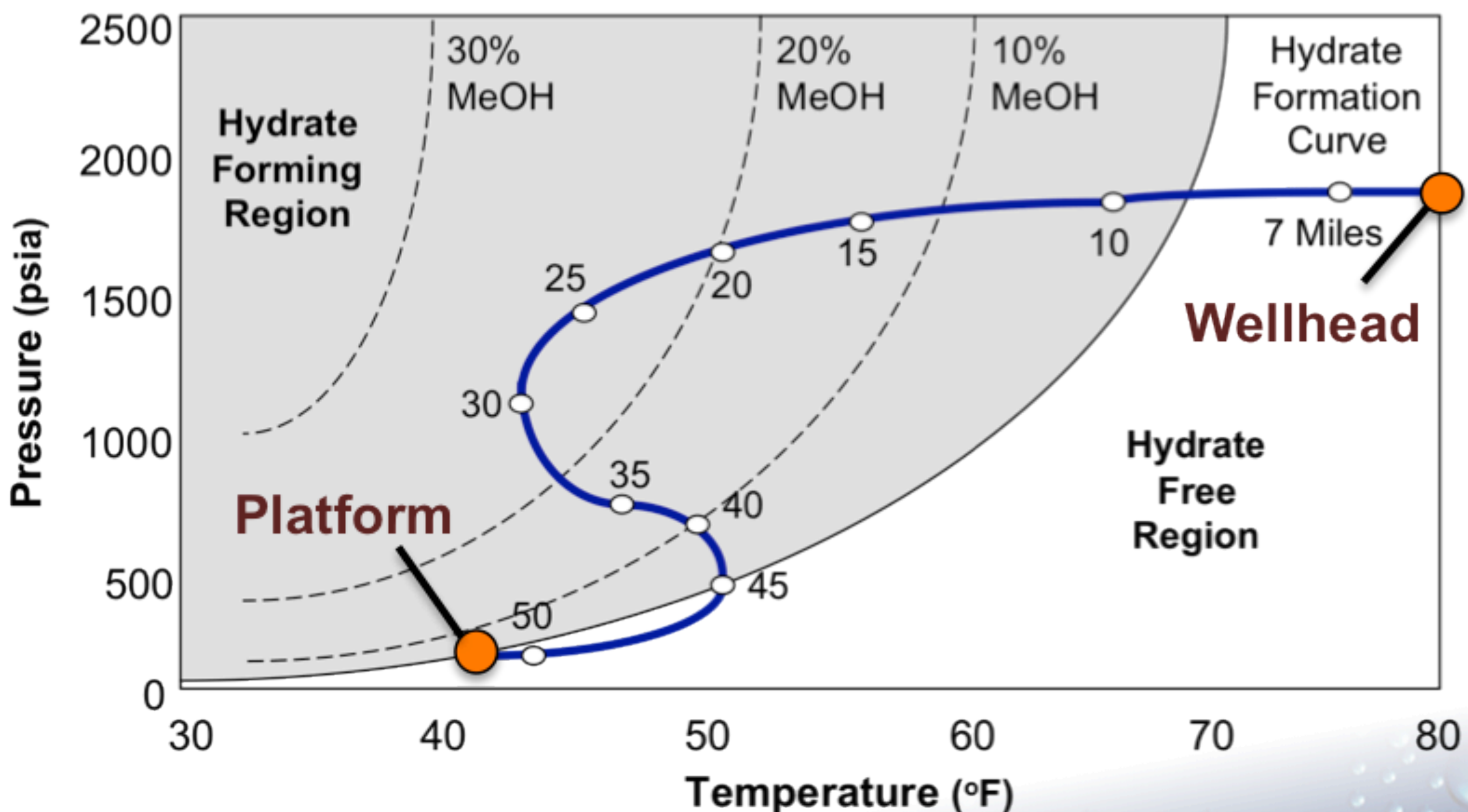
- **Risk based approach**
- **Sound engineering practice/design**
- **Understand effect of water and hydrates in production system**
- **Need to combine field experience with laboratory research**

Modified from K. Kinnari (Statoil)

Hydrates in Flow Assurance

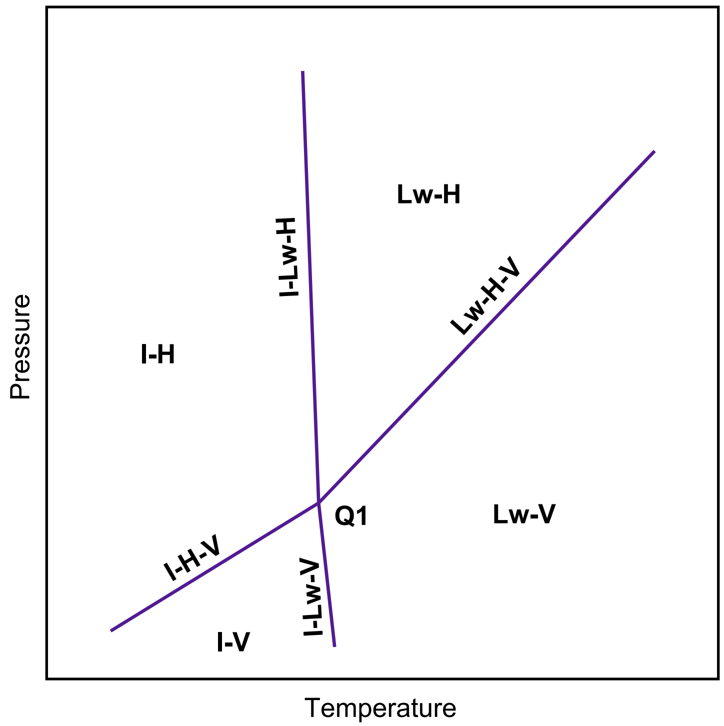
Hydrate Avoidance (inhibitor injection)

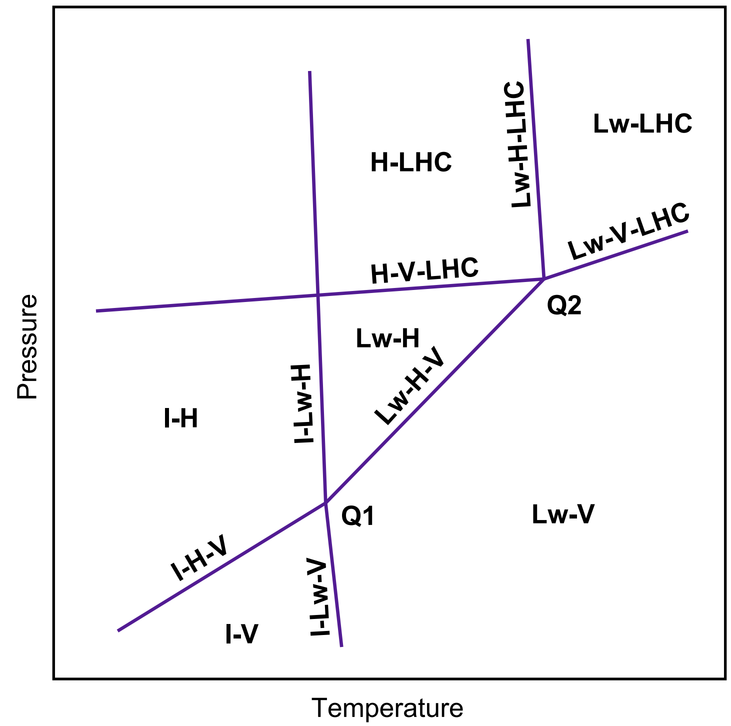
Determine hydrate phase stability boundary



Typical Hydrate Phase Diagram

Hydrates are a mixture by definition,
but their phase behavior is the same as a simple component





Quadruple point Q1
I-Lw-H-V

Quadruple point Q2
Lw-H-V-LHC

Gibbs Phase Rule

$$F = C - P + 2$$

F: degrees of freedom (intensive variable)

C: number of components

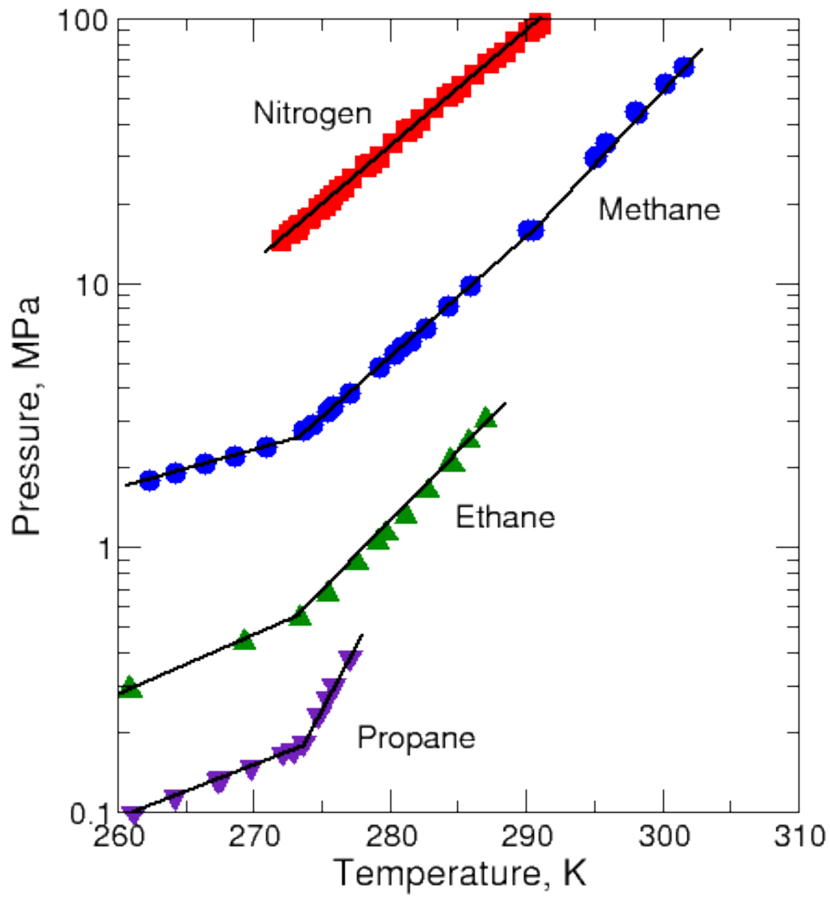
P: number of phases

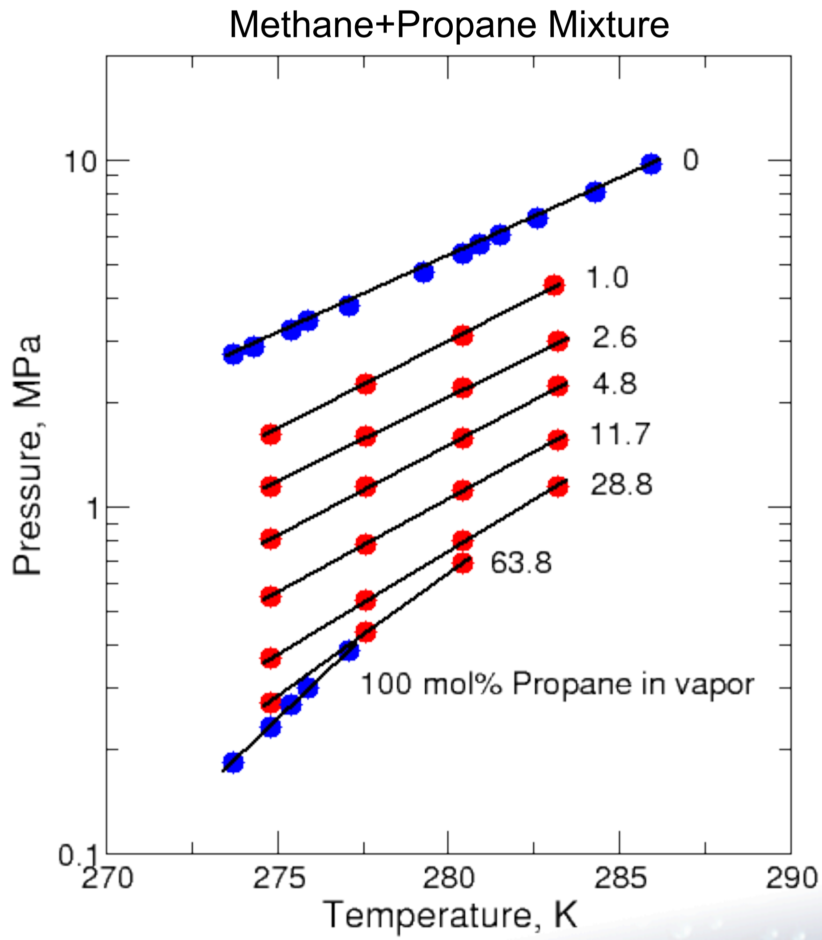
Example:

2 components, 2 phases :: F = 2

4 components, 3 phases :: F = 3

Typical Hydrate Phase Diagram





Hydrate Avoidance: Inhibitor Injection

Most common THI (thermodynamic Hydrate Inhibitor):
Methanol (MeOH), Ethanol (EtOH), Monoethylene glycol (MEG)

Hydrate inhibitor	Methanol (MeOH)	Monoethylene glycol (MEG)
Advantages	Easily vaporized into gas For flowline and topside plugs No salt problems	Relatively recoverable For plugs in wells and risers Low gas and condensate solubility
Disadvantages	Costly to recover High gas and condensate losses Poisons molecular sieves, catalysts; downstream problems	High viscosity inhibits flow Boiler fouling, salt precipitation

Hydrate Avoidance: Inhibitor Injection

Most common THI (thermodynamic Hydrate Inhibitor):
Methanol (MeOH), Ethanol (EtOH), Monoethylene glycol (MEG)

	MeOH	MEG
In water, lb_m/MMSCF	174.4	313.1
In gas, lb_m/MMSCF	34.2	0.006
In condensate, lb_m/MMSCF	0.8	0.0061
Total, lb_m/MMSCF	209.4	313.11
Total, gal/MMSCF	31.5	33.3

Hydrate Avoidance: PAST to PRESENT

- Focus on hydrate phase equilibrium boundary
- Under which conditions will hydrates form?
- If hydrates can form, how can they be inhibited?
- Thermodynamic hydrate inhibitions (methanol, MEG)
- Insulation
- Direct Electrical Heating

Hydrate Avoidance works!

Hydrates in FA: PRESENT to FUTURE

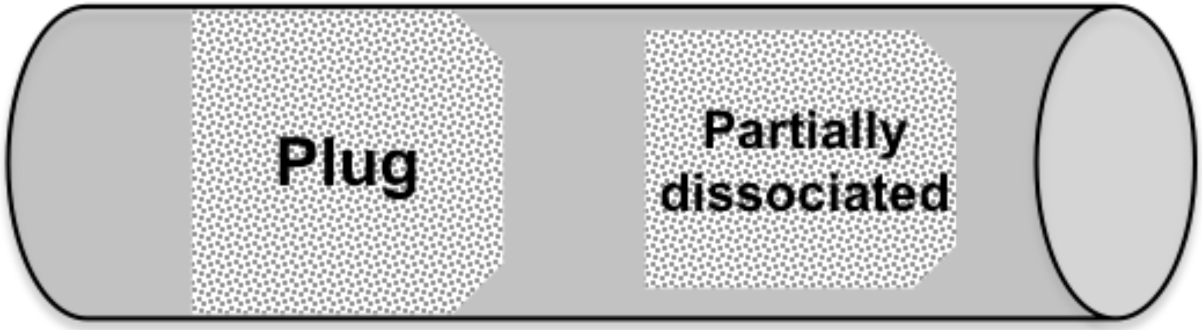
- Impractical ($$ and logistic) to completely avoid hydrates
- Must live with hydrates
- Management of hydrates
  - chemical treatment
  - monitoring
  - remediation

Must have good knowledge of how, when, where, how much hydrates are formed

Hydrate Management

Hydrate Remediation

How to safely remove a hydrate plug



Need to establish pressure communication in the flowline

- **Two-side depressurization**
- **One-side depressurization**
- **Electrical heating**
- **Coil tubing**
- **Chemical treatment**

Heat of Formation/Dissociation (ΔH_d)

- Latent heat of transformation for hydrates
  - Formation: exothermic
  - Dissociation: endothermic
  - *Must input heat to remove hydrate plug in pipelines!*

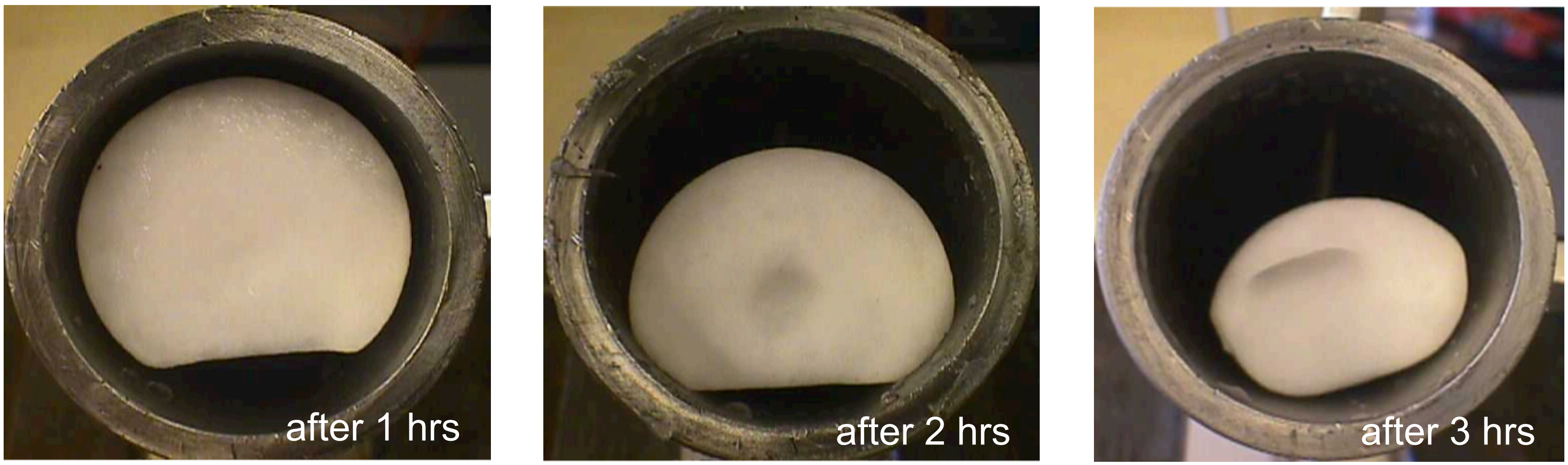
- Latent heat depends upon guest and occupancy

	$H \Leftrightarrow L + G$
CH_4:	54.2 kJ/mol
C_2H_6:	71.8 kJ/mol
C_3H_8:	129.2 kJ/mol

Values are per mole of guest

Hydrate Management

Hydrate Remediation

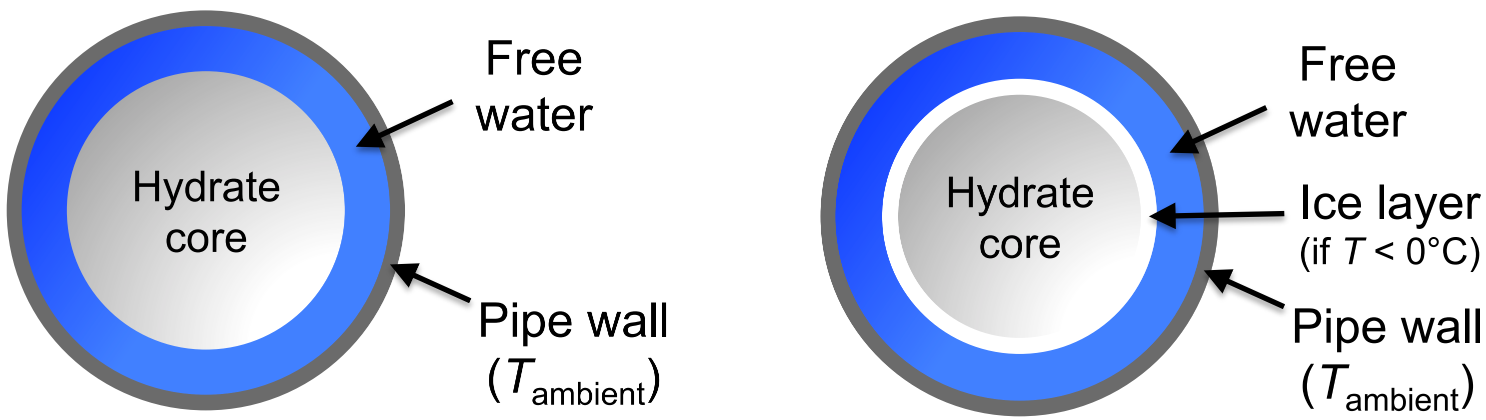


Hydrate plug dissociation is predominantly radial, as opposed axial

Hydrate Management

Hydrate Remediation

Hydrate plug dissociation/removal

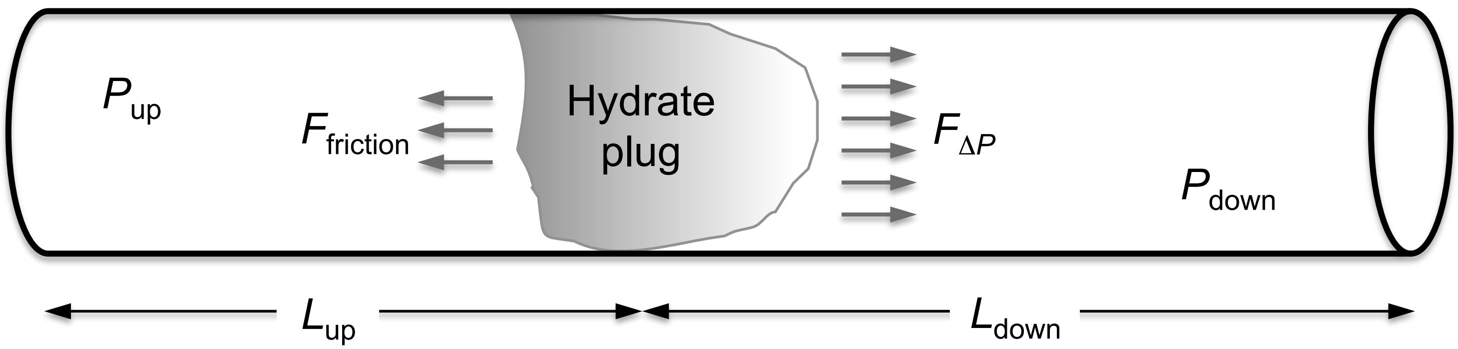


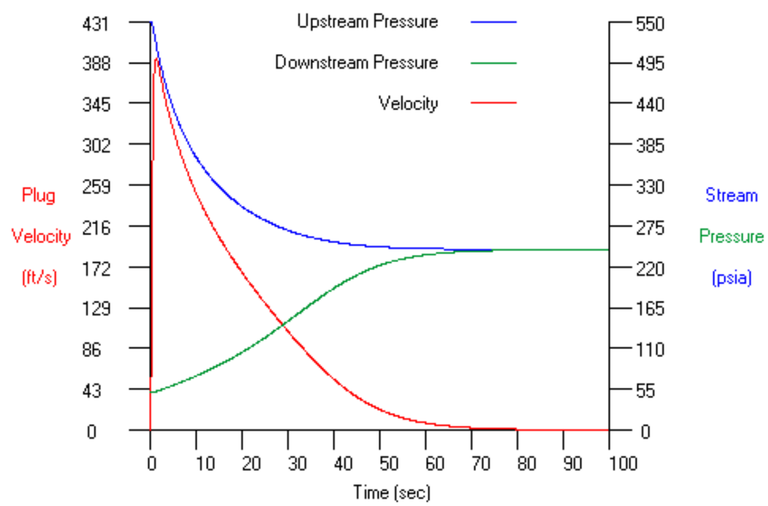
- **Partial dissociation (create annulus)**
- **Allow for pressure communication and chemical treatment**

Hydrate Management

Hydrate Remediation

Need to determine plug location and displacement



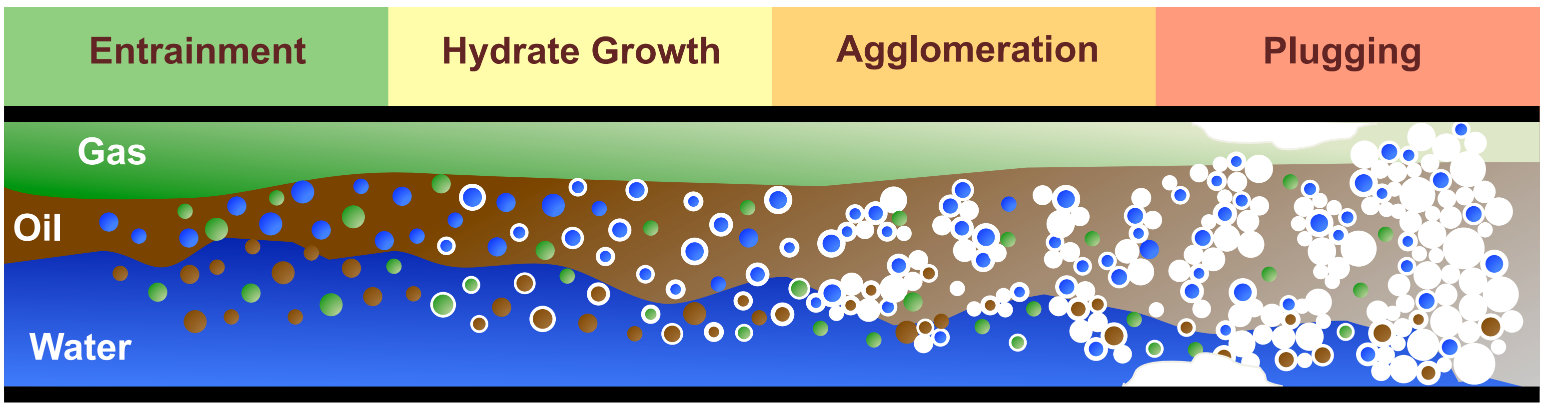


- If plug dislodges, how far/ fast will it travel?
- Can the pipeline burst?

Hydrate Management

Model Hydrates in Multiphase Flow

Gas, Oil, Water (free, emulsified, dispersed)



Emulsification/ Dispersion

Nucleation

Growth

Rheology

Co/Ad-hesion

Aggregation

Deposition

Jamming/ Bedding

Must account for each phenomenon combined with multiphase flow

Hydrate Management

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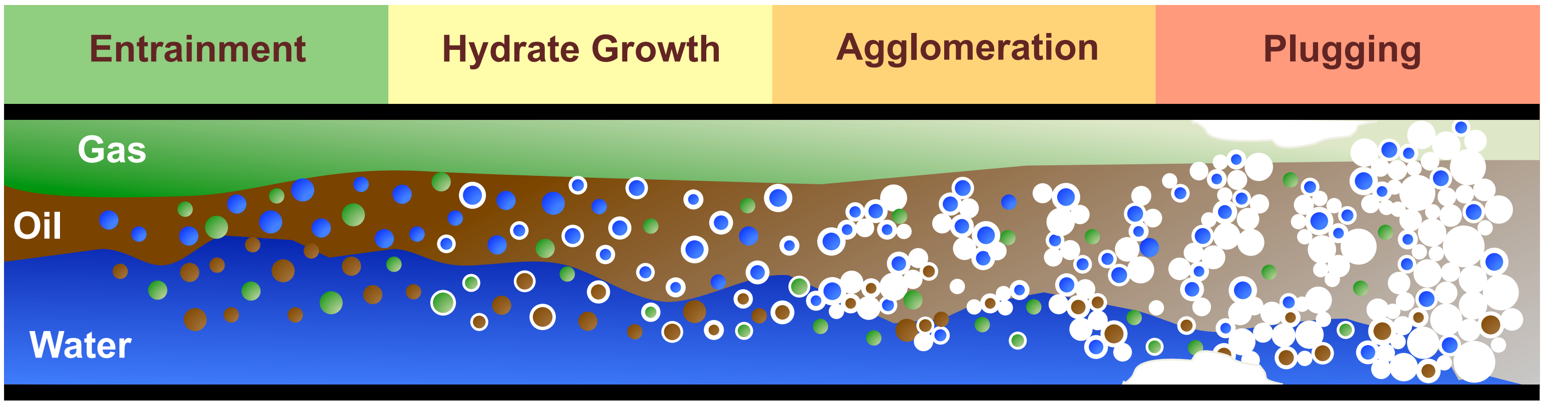

Emulsification/ Dispersion

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Co/Ad-hesion

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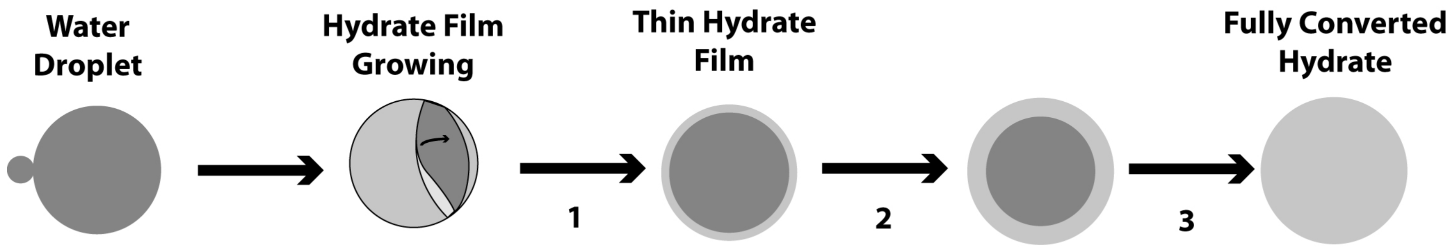
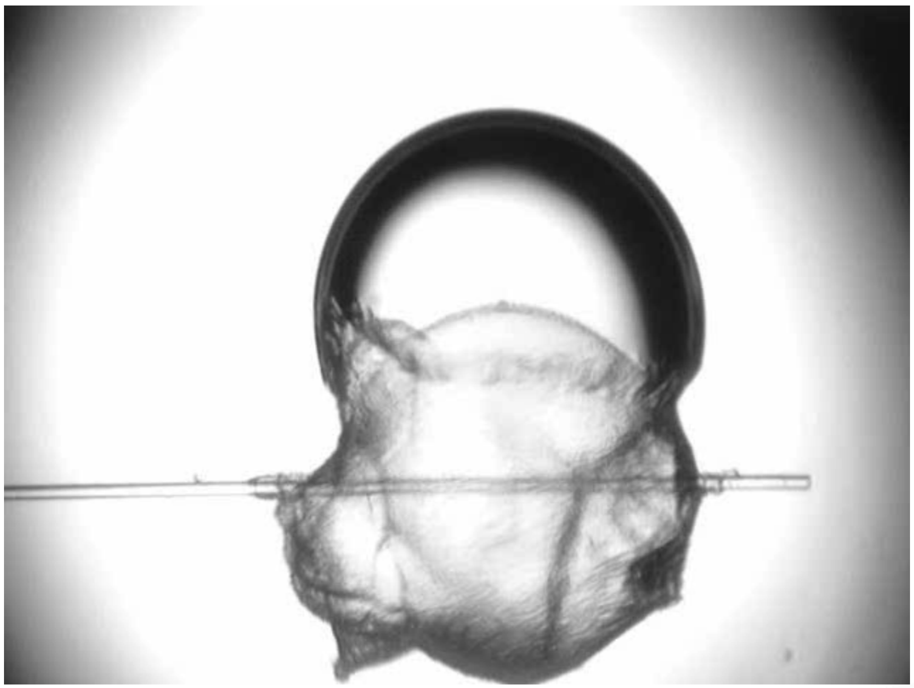
Hydrate Grows at the Interface

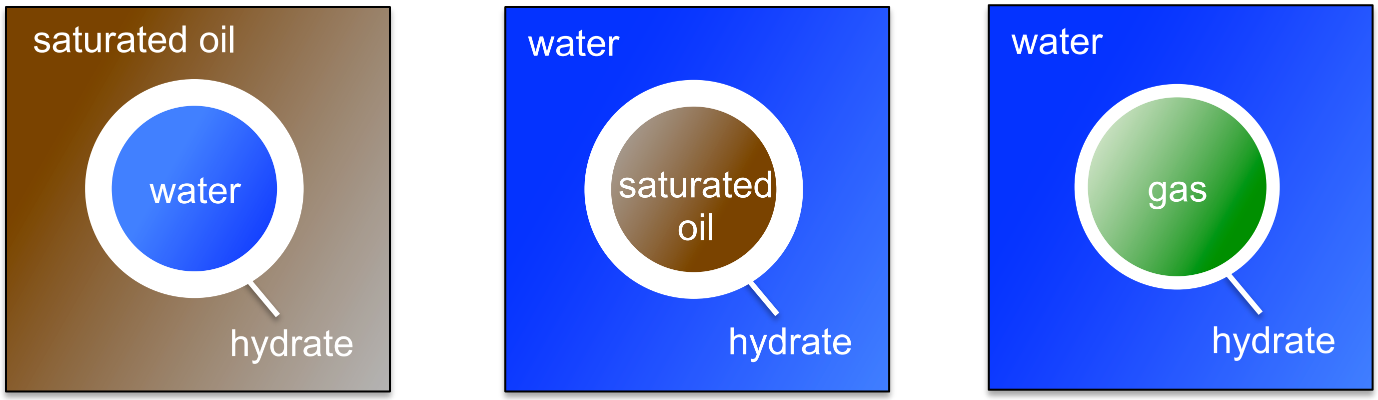




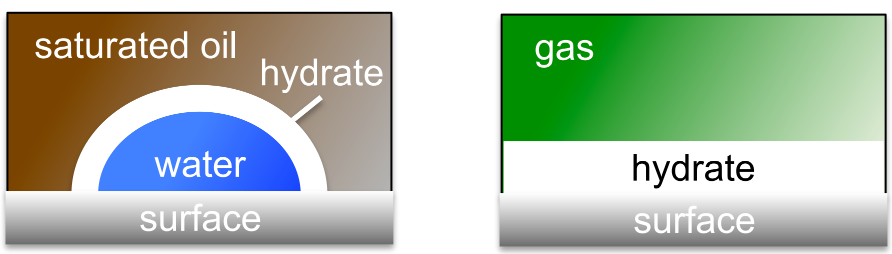
Hydrate growth on water droplet in contact with another hydrate particle (CyC5 hydrate)

Hydrate Growth at Interfaces

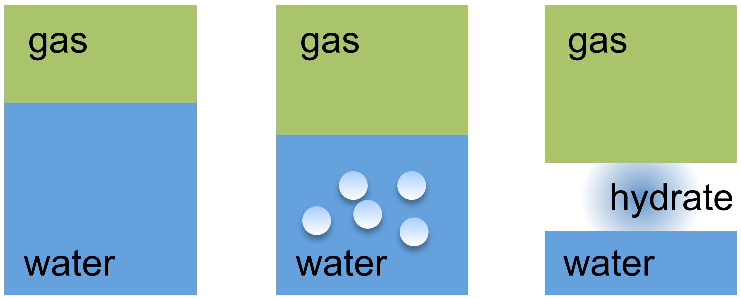
Formation in the bulk

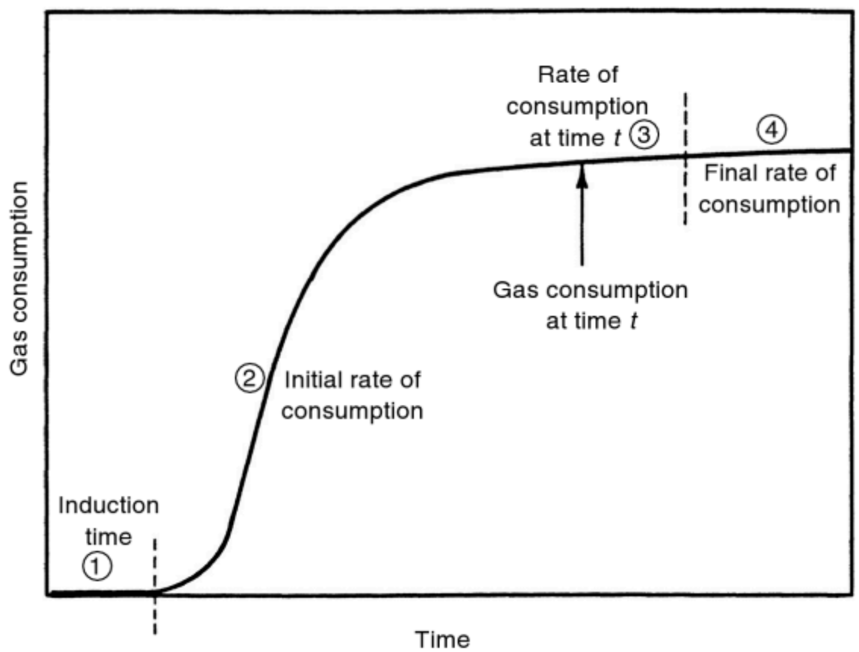


Formation on the wall/surface



Hydrate Formation Rate





Induction time: metastable system

Growth can be limited by:

- **Intrinsic growth kinetics** (limited by rate of formation/ driving force)
- **Mass transfer** (limited by contact of gas and water)
- **Heat transfer** (limited by removal of heat from system)

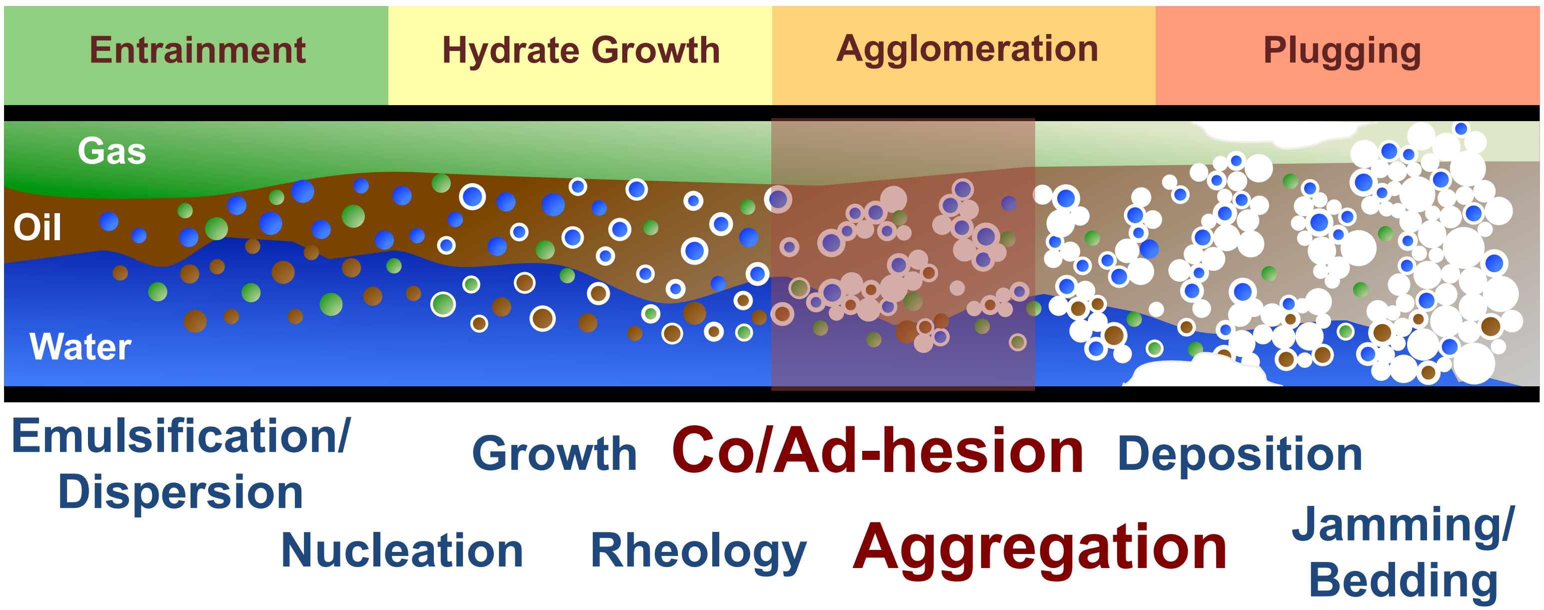
CH_4 solubility in water: ~ 1:4000
CH_4 in hydrate: ~ 1:6

CH_4 hydrate ΔH_f = +54.2 kJ/mol

Hydrate Management

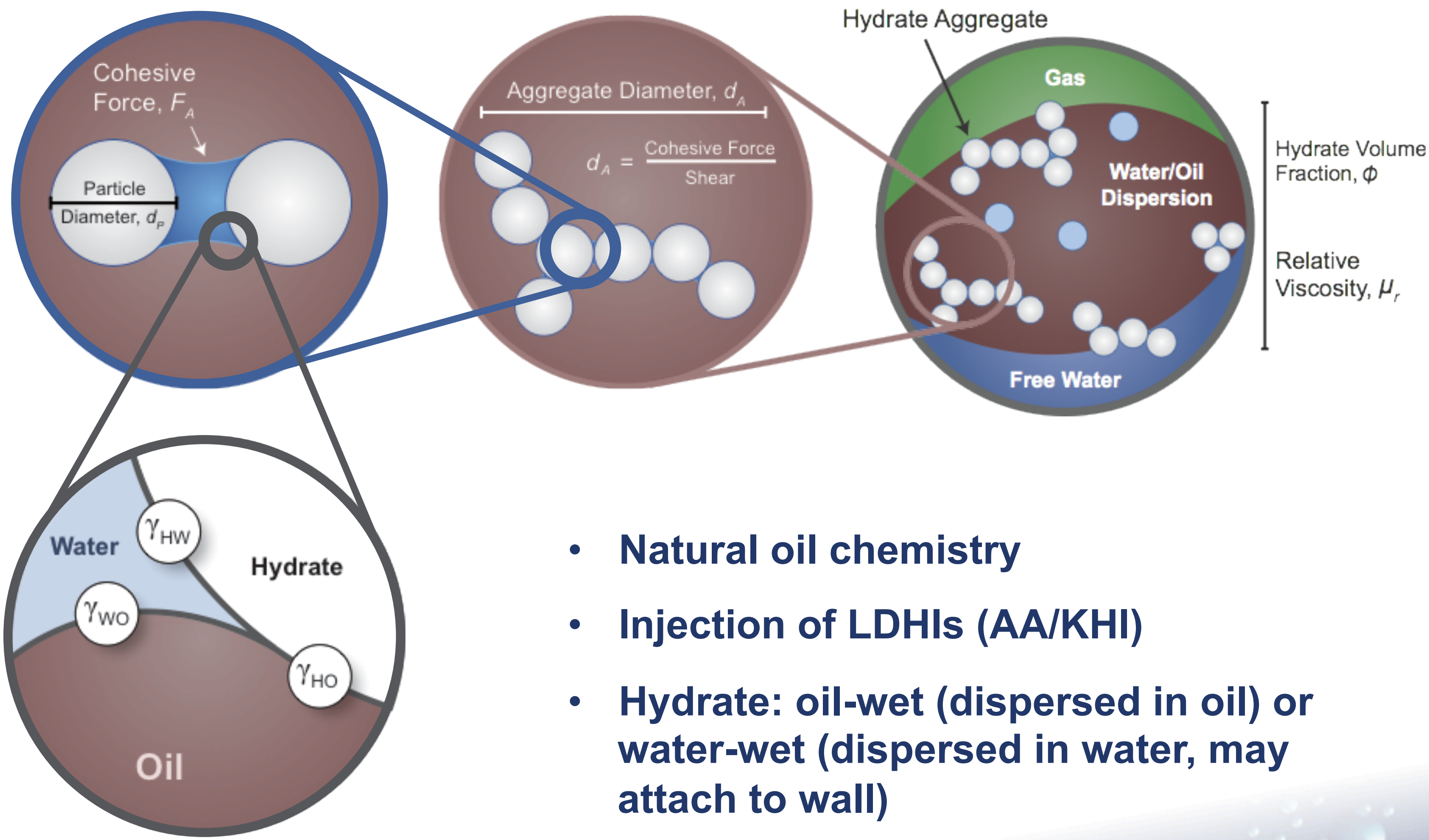
Model Hydrates in Multiphase Flow

Gas, Oil, Water (free, emulsified, dispersed)



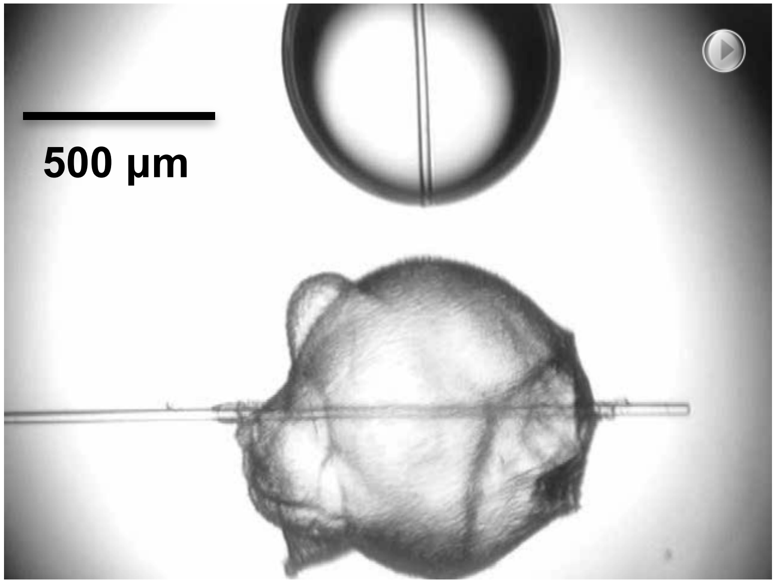
Preventing agglomeration is key to avoid plugging

Hydrate Interfacial Interactions



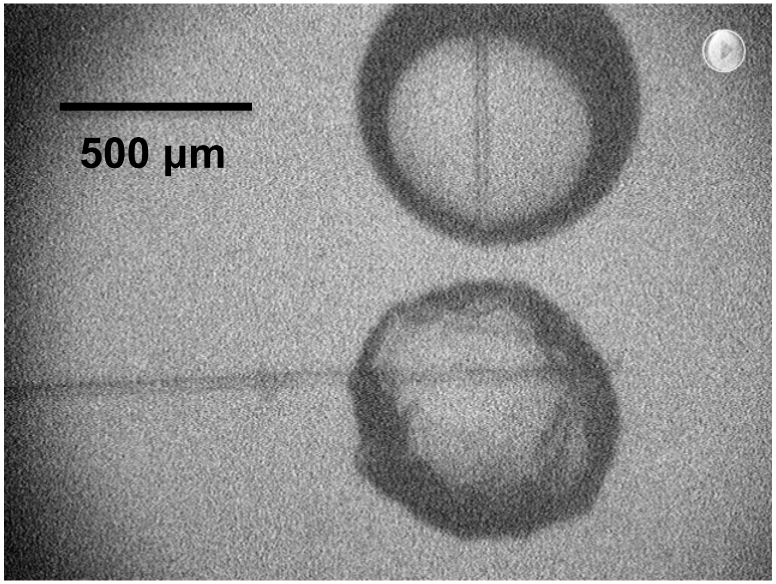
- **Natural oil chemistry**
- **Injection of LDHIs (AA/KHI)**
- **Hydrate: oil-wet (dispersed in oil) or water-wet (dispersed in water, may attach to wall)**

Crude Oil Prevents Water from "Jumping" onto Hydrate Particle



Hydrate-Water Droplet in Pure Cyclopentane (2.7°C)

Video begins after 1 minute; spans 5 minutes

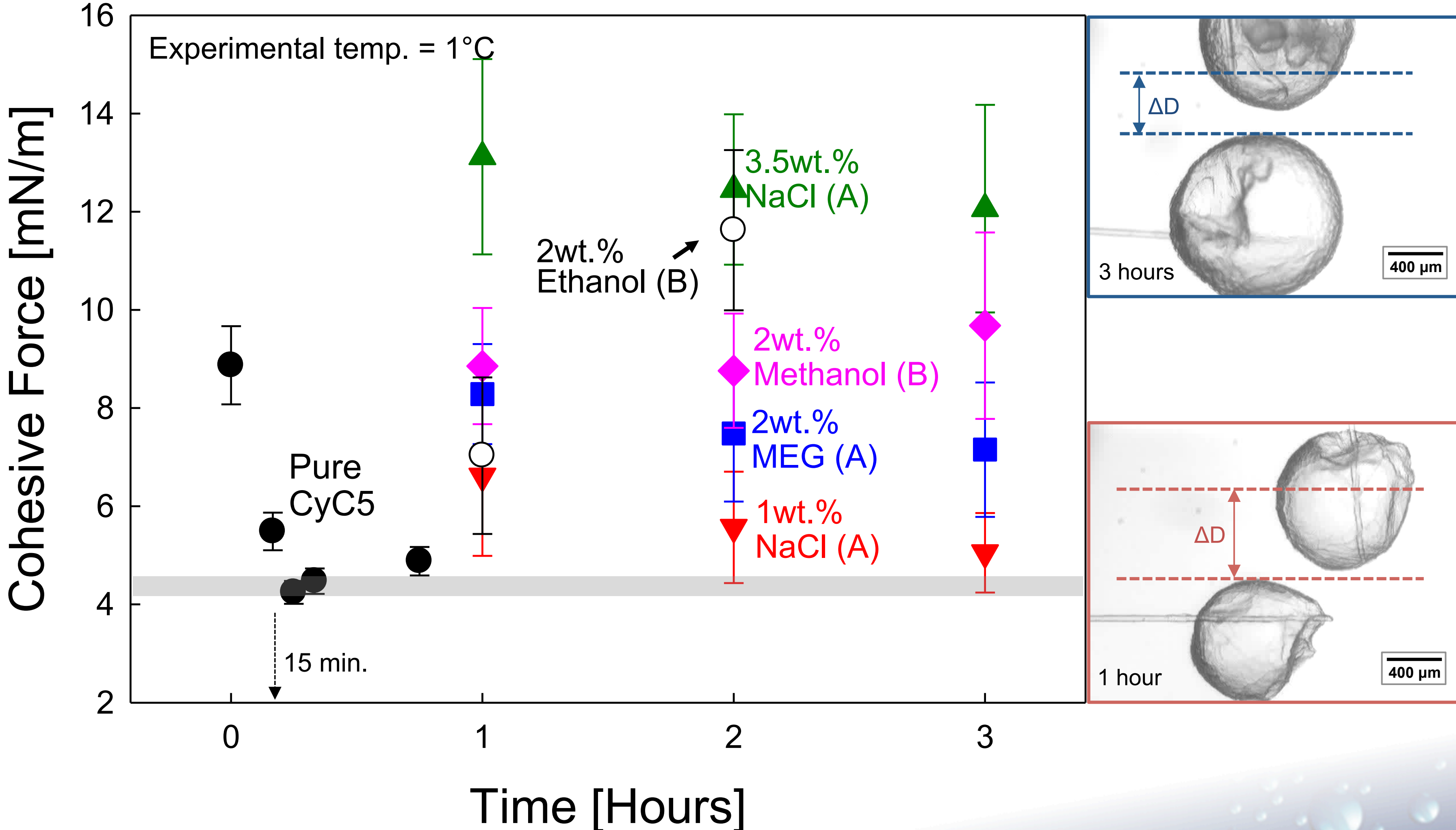


Hydrate-Water Droplet in 5 wt% crude oil (2.7°C)

Video begins after 30 minutes; spans 15 minutes

After 45 minutes of contact, NO adhesion with crude oil

Cohesion Force for Hydrate Particles



Measurements performed in the Micromechanical Force Apparatus

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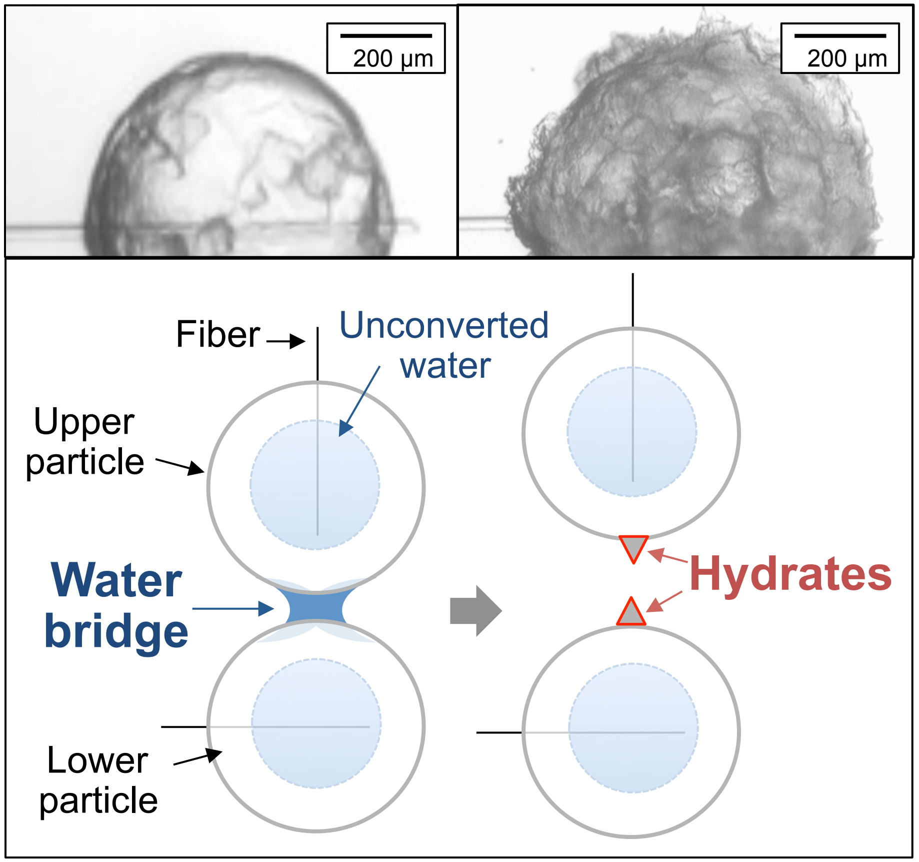
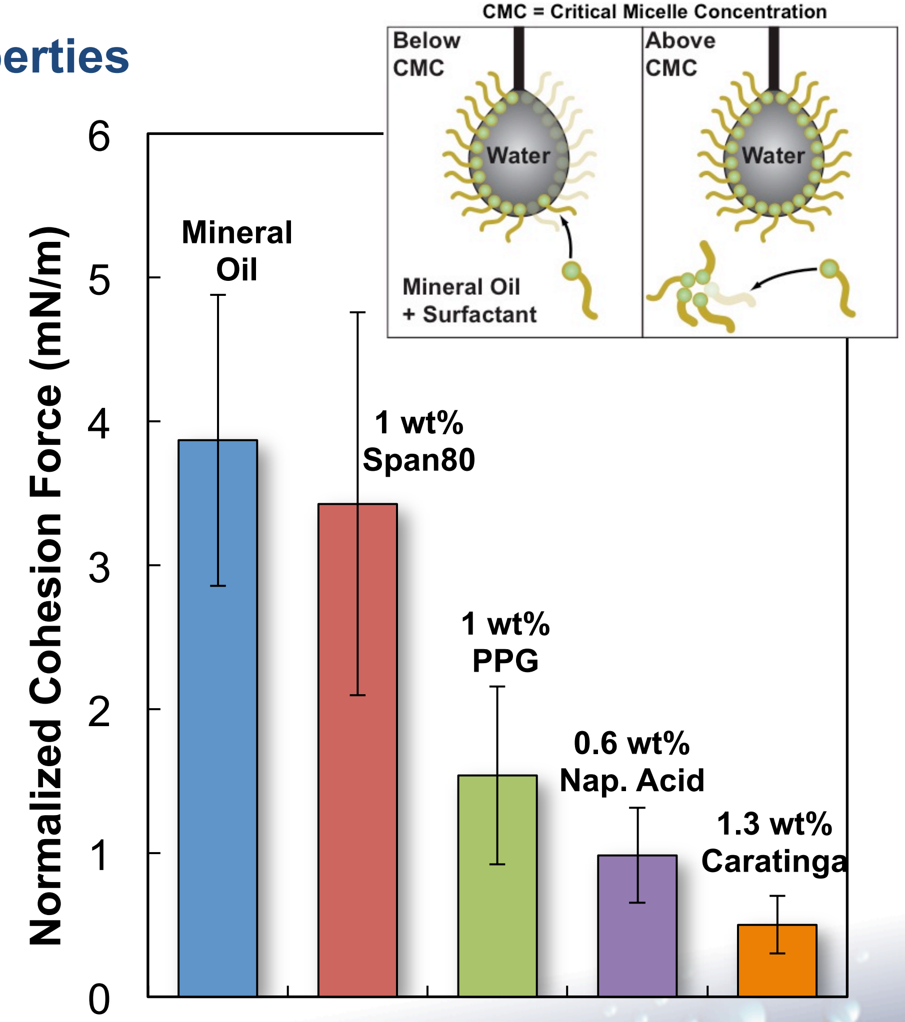
Interfacial Properties of Hydrate Particles

Physical and Chemical Interfacial Properties





Hydrate Agglomerate Diameter - d_A

Force balance between inter-particle and shear forces

$$\left(\frac{d_A}{d_P}\right)^{4-f} - \frac{F_a\left[1-\frac{\phi}{\phi_{\max}}\left(\frac{d_A}{d_P}\right)^{3-f}\right]^2}{d_P^2\mu_0\dot{\gamma}\left[1-\phi\left(\frac{d_A}{d_P}\right)^{3-f}\right]} = 0$$

- d_A - hydrate agglomerate diameter
- d_P - hydrate particle diameter
- ϕ - hydrate particle volume fraction
- ϕ_{max} - maximum packing fraction (= 4/7)
- f - fractal dimension
- F_a - interparticle force (F_a/R = 50 mN/m)
- μ_0 - oil viscosity
- γ - shear rate

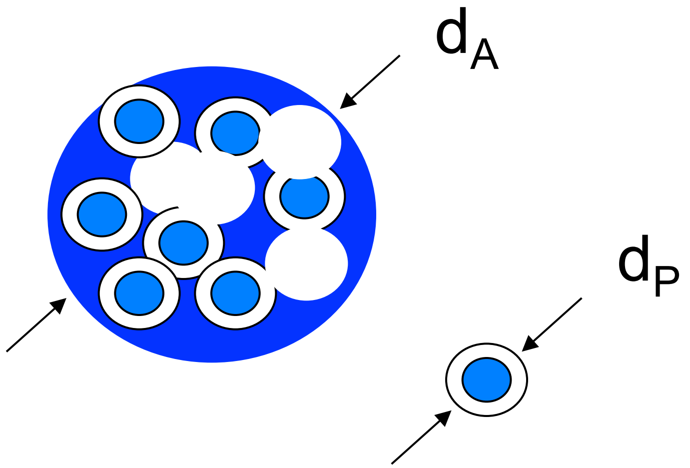
Solve for d_A - hydrate agglomerate diameter

(Camargo and Palermo, 2002)

Effective Hydrate Volume Fraction

Particle volume fraction + entrapped fluid fraction

$$\Phi_{eff} = \Phi \left(\frac{d_A}{d_P} \right)^{(3-f)}$$



d_A - hydrate agglomerate diameter

d_P - hydrate particle diameter

Φ - hydrate particle volume fraction

f - fractal dimension

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HYDRATES SCIENCE to ENGINEERING

Relative Viscosity

- Relative viscosity between oil and hydrate slurry
- Relative viscosity is a function of
  - particle volume fraction and size
  - attractive force, shear rate, and viscosity

$$\mu_r = \frac{1-\Phi_{eff}}{\left(1-\frac{\Phi_{eff}}{\Phi_{\max}}\right)^2}$$

Φ - effective particle volume fraction

Φ_{max} - maximum packing fraction (= 4/7)

μ_r - relative viscosity

(Mills, P. J., de Physique Letters, 1985)

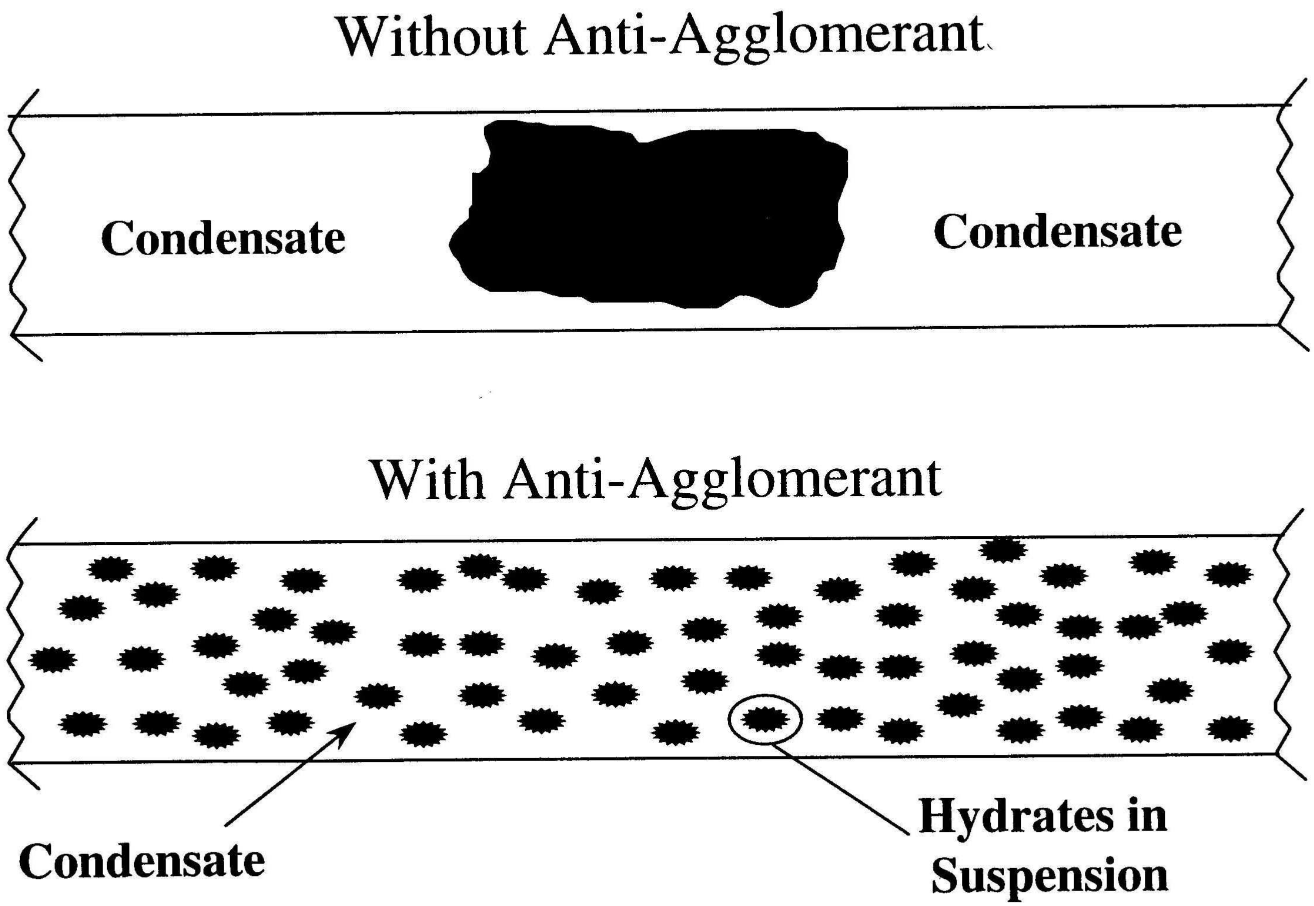
Hydrate Management

Chemical injection of Low Dosage Hydrate Inhibitors (LDHIs)

Anti-Agglomerants (AAs)

- Used in oil systems
- Effective for low water cut system (< ~40%)
- Quaternary ammonium salts
- Used in low concentration, ~1-2 wt%
- Convert all (most) water to hydrate
- Prevent hydrate particles from agglomerating
- Good for high temperature, shut-in and restart of line
- Significant environmental concerns on disposal

Anti-Agglomerant in Pipeline



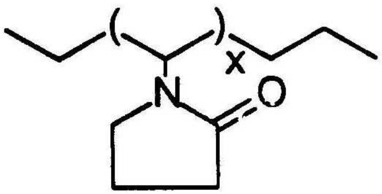
Hydrate Management

Chemical injection of Low Dosage Hydrate Inhibitors (LDHIs)

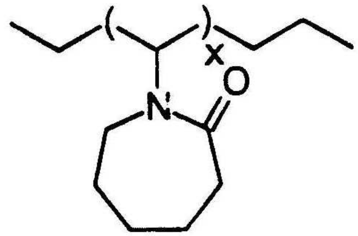
Kinetic Hydrate Inhibitors (KHIs)

- Water soluble chemicals
- Used in oil and gas systems
- Used in low concentration, ~1-2 wt%
- Allow initial hydrate crystal to form, prevent growth
- Limited to low subcooling (ΔT < ~10 °C)
- Not for shut-in and restart operation
- Significant environmental concerns on disposal, water quality

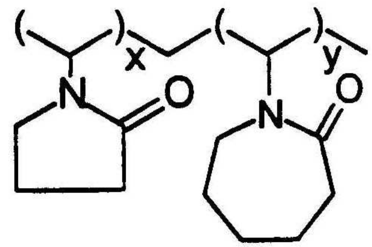
Chemical Structures for Some KHIs



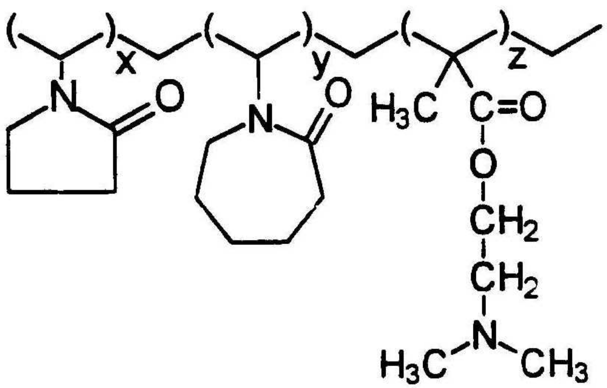
PVP



PVCap



Poly(VP/VC)



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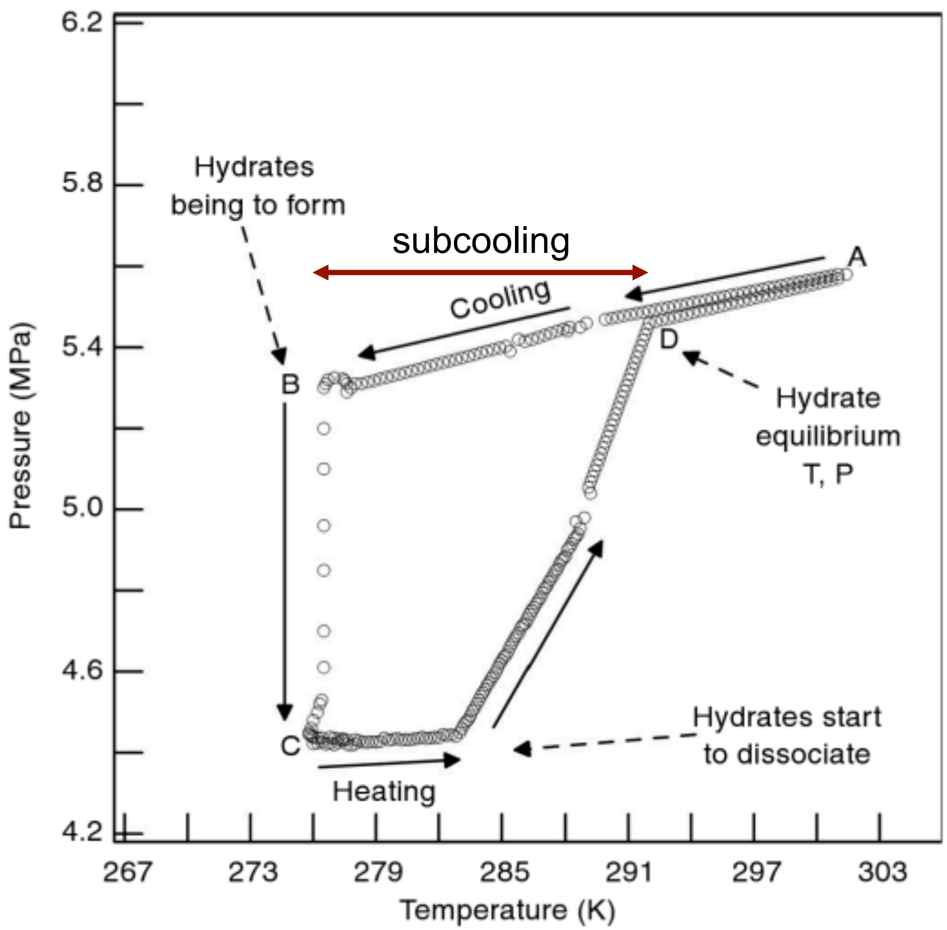
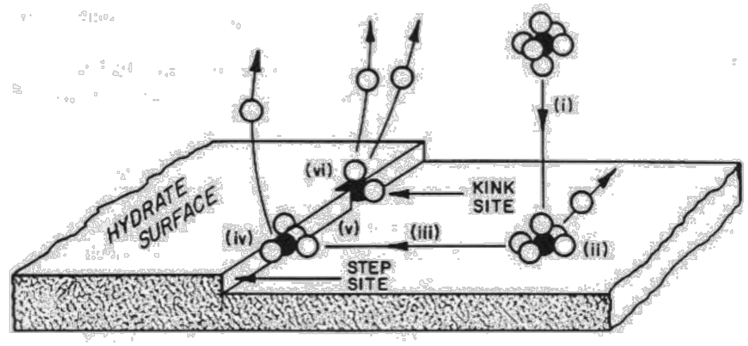
Mechanism for how these KHIs work is unknown

Hydrate Formation and Subcooling



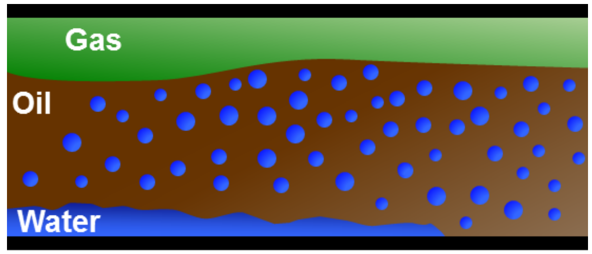
System need to be subcooled for hydrates to form (metastability due to liquid-solid transition)

KHIs tend to extend time system stay in metastable conditions



Mechanism hypothesis: KHI adsorbs on crystal surface

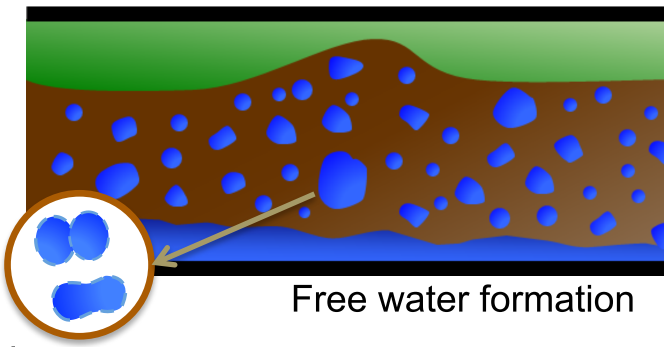
Hydrate Management for Shut-in/Restart



Steady state flow
(dispersed water droplets)

'No-Touch' time

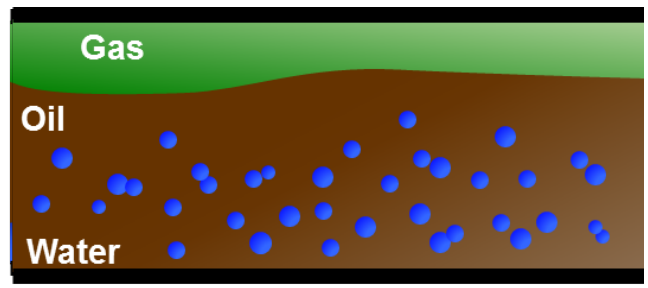
Unstable emulsion



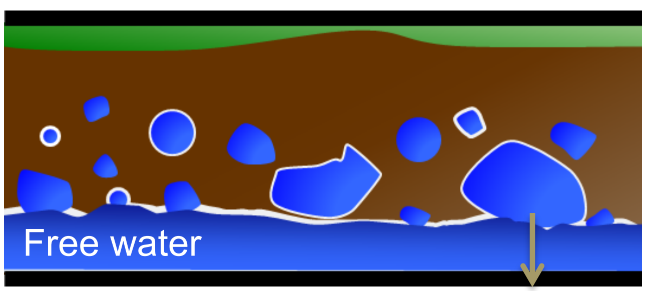
Free water formation

Coalescence

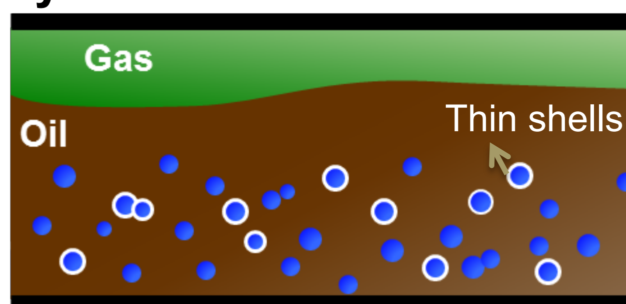
Stable emulsion



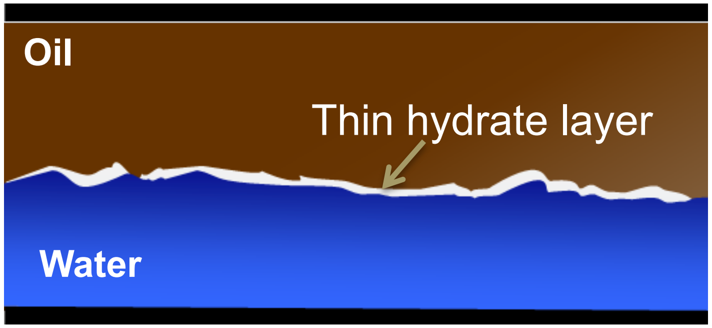
Within hydrate stability zone



Larger water droplets
with thin hydrate shell

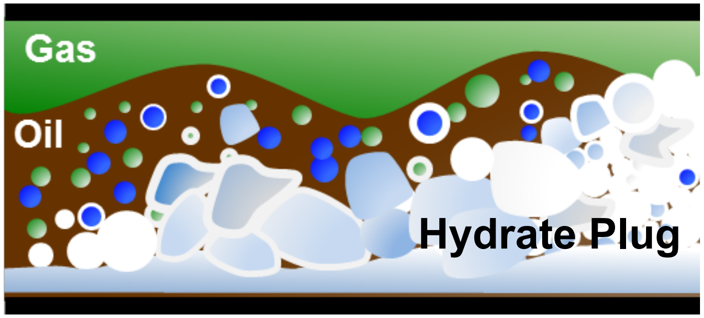


Hydrate Management for Shut-in/Restart



- Phase separation after long shut-in
- Thin hydrate layer on the free water
- Very slow process (no shear)

- Systematic opening of valve
- Introduction of gas bubbles from well
- Rapid formation of hydrates

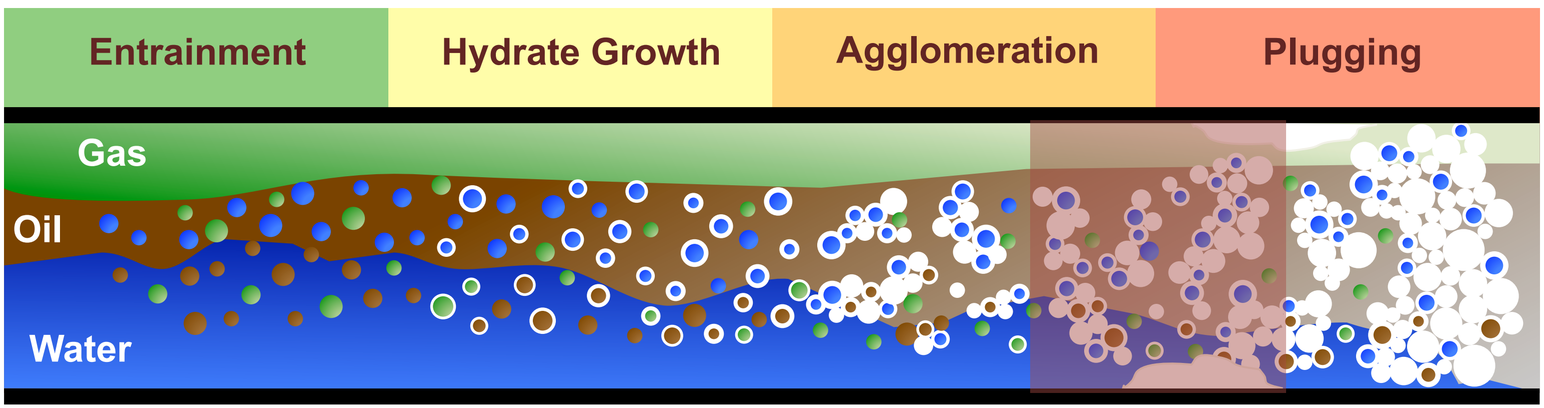


- Free water conversion to hydrates
- Gas bubbles conversion to hydrates
- Rapid plug formation before hot fluids from wellhead reach the plug location

Hydrate Management

Model Hydrates in Multiphase Flow

Gas, Oil, Water (free, emulsified, dispersed)



Emulsification/ Dispersion

Nucleation

Growth

Rheology

Co/Ad-hesion

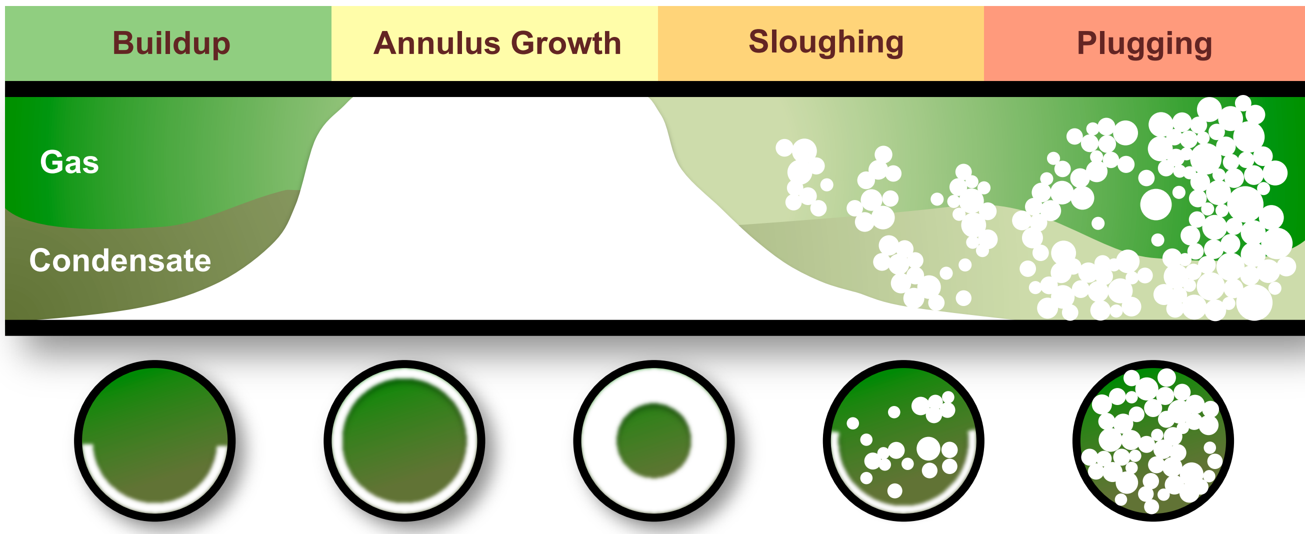
Aggregation

Deposition

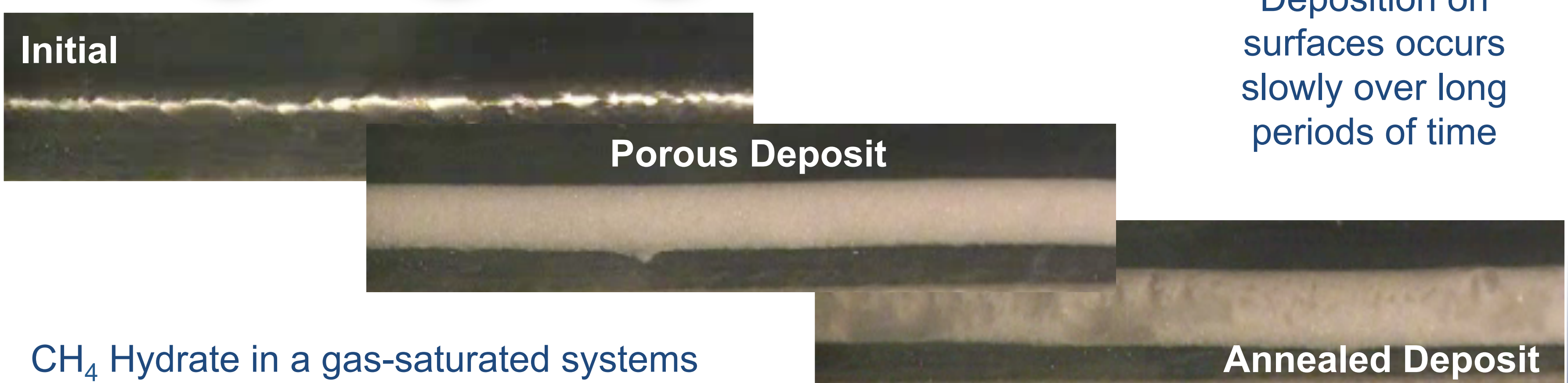
Jamming/ Bedding

Hydrate Deposition (Gas systems)

Gas / Gas Condensate (no free water)



Deposition on surfaces occurs slowly over long periods of time



CH_4 Hydrate in a gas-saturated systems at 100 bar (cold surface at 0.5 °C)

Hydrate Deposition from Gas Phase

Condensed water immediately converted to hydrates
Porous hydrate anneals to become hard deposit

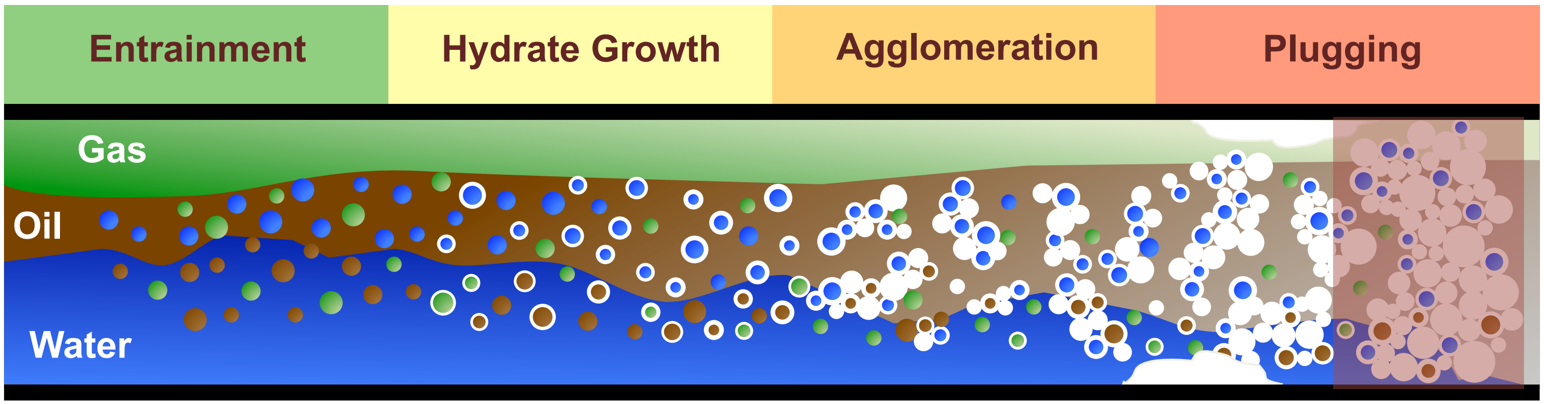
Hydrate Deposition from Gas Phase

How to prevent/minimize hydrate deposition on surfaces?

- Remove all water from gas (near impossible)
- Keep surface warm (insulation, heating)
- Coat inside surface (hydrophobic coating)
- Periodically scrap surface (pigging)

Conceptual Model for Hydrates in Multiphase Flow

Gas, Oil, Water (W/O and O/W Emulsions, Free)

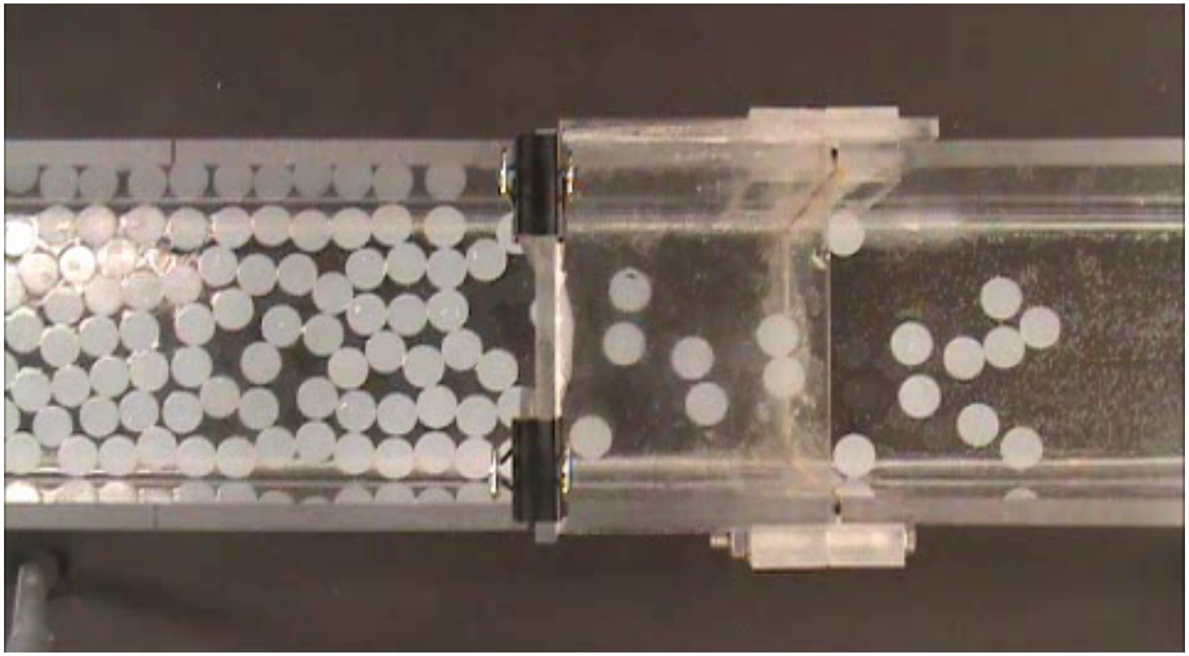


Emulsification **Growth** **Co/Ad-hesion** **Deposition**

Nucleation **Rheology** **Aggregation** **Jamming**

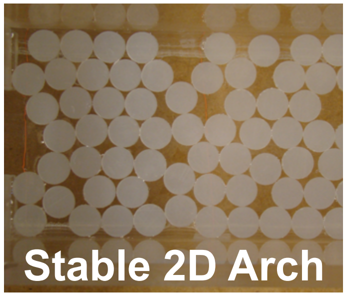
Each phenomenon studied separately

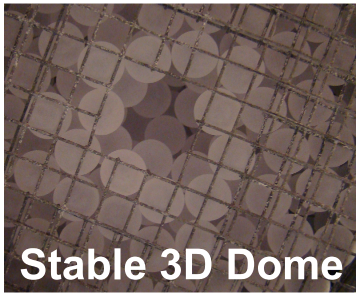
Particle Jamming in Flowing Systems



Three Ingredients:

- Dense particle flow
- Flow restriction
- $d_o/d_p = R$ is small

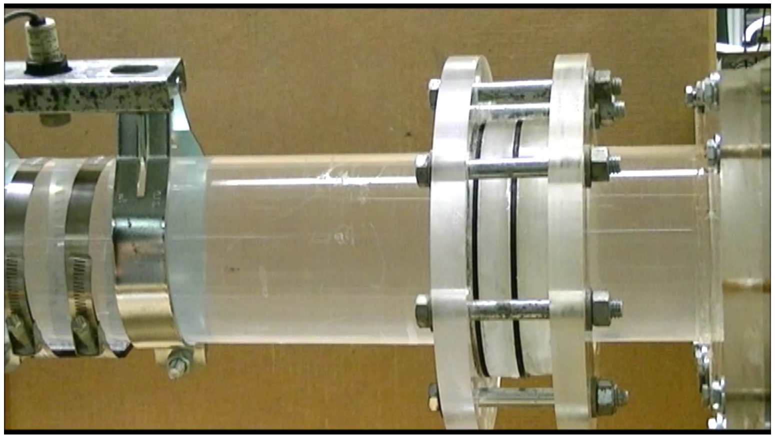




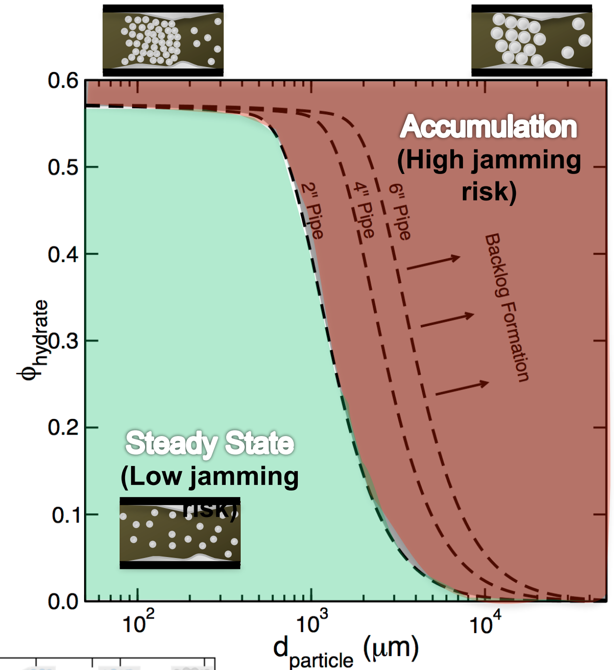
Variables:

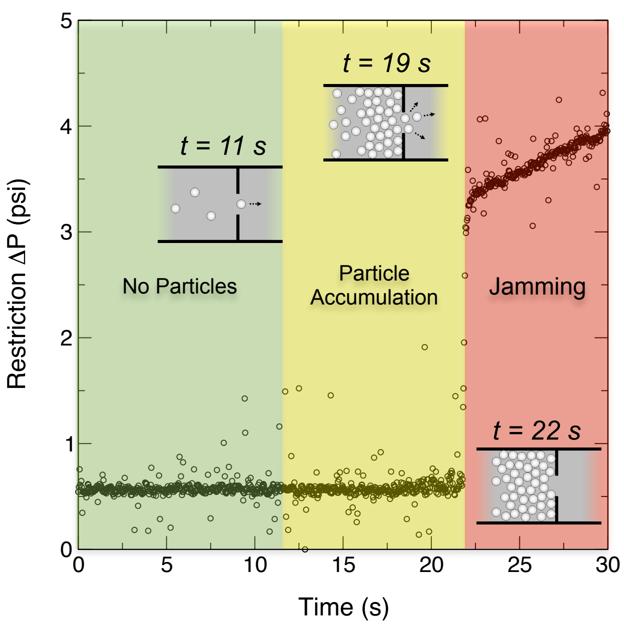
- Particle size/shape
- Restriction size/shape
- Fluid velocity
- Particle concentration

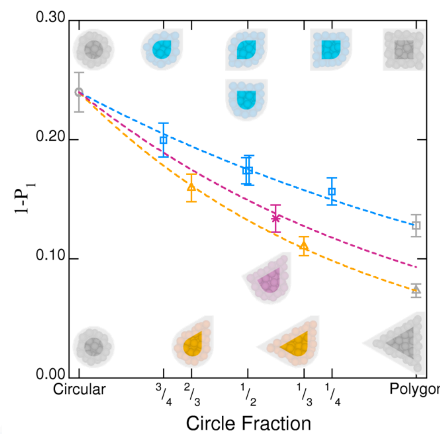
Particle Jamming in Flowing Systems



Jamming Probability Map







Survival Probability

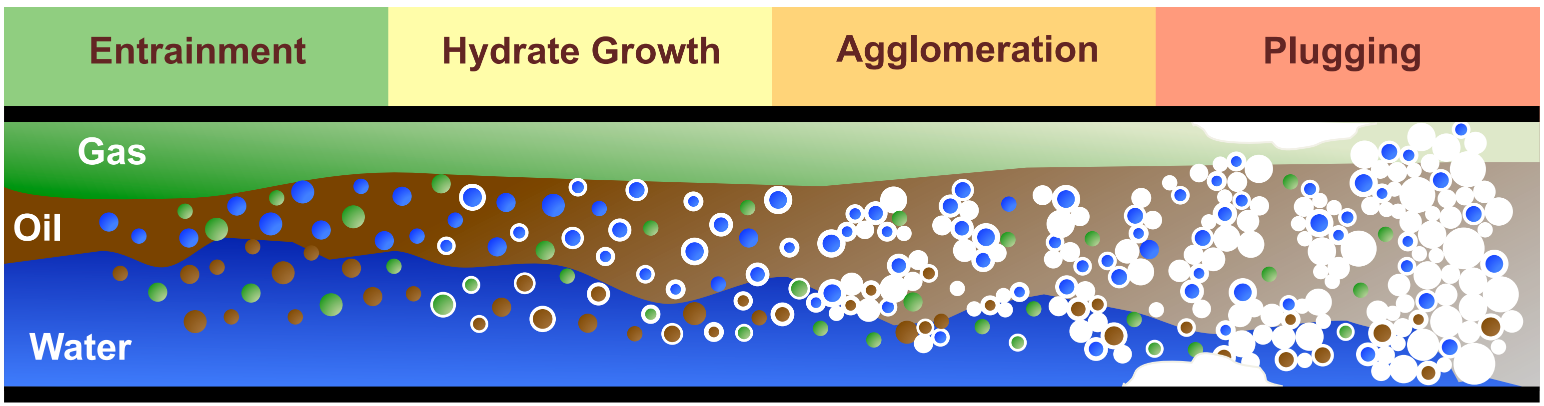
$$\ln\left[S(\tau)\right] = -\int_0^{\tau} \Lambda d\tau$$

Jamming in any geometry

Hydrate Management

Model Hydrates in Multiphase Flow

Gas, Oil, Water (free, emulsified, dispersed)



Emulsification/ Dispersion

Growth

Co/Ad-hesion

Deposition

Nucleation

Rheology

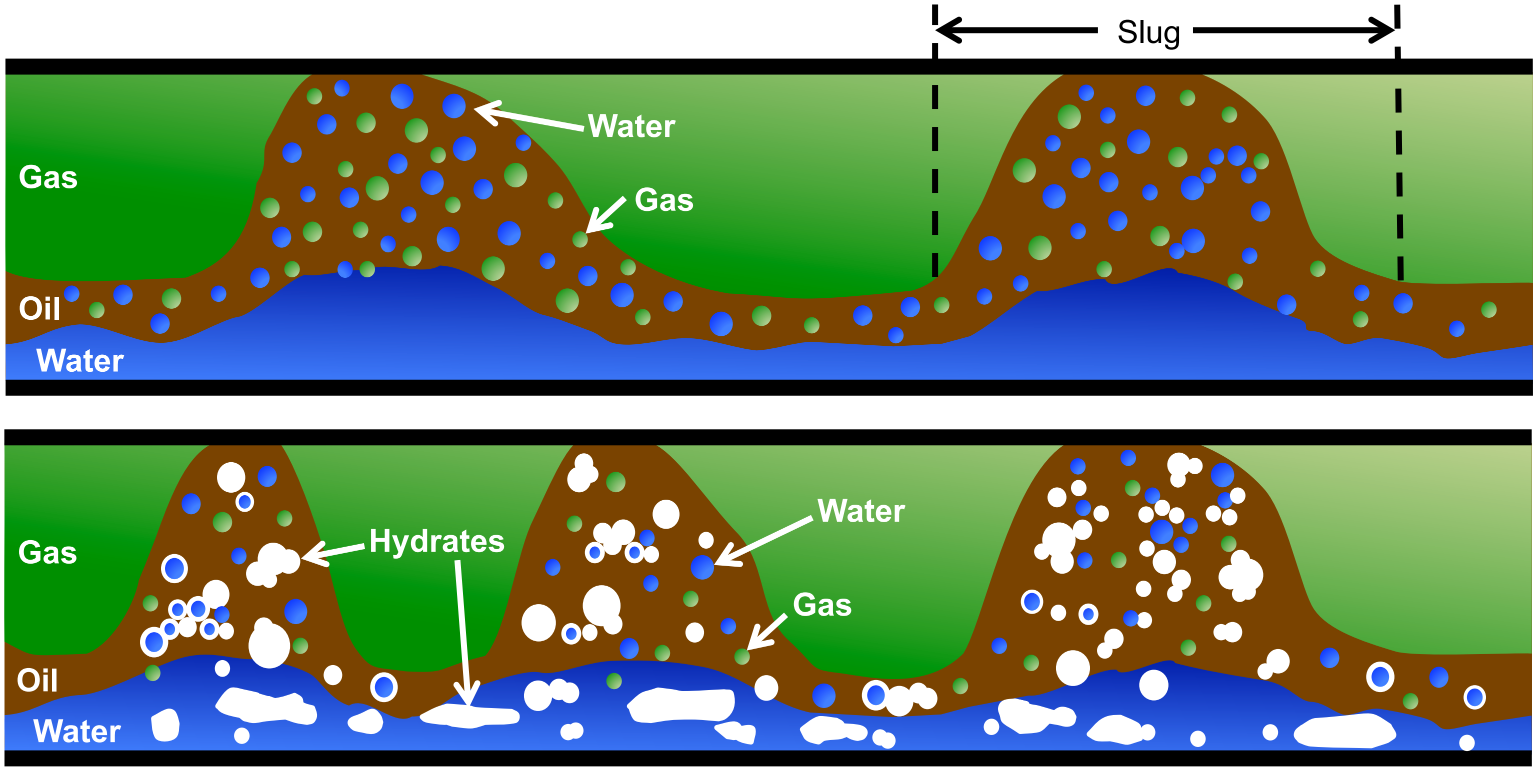
Aggregation

Jamming/ Bedding

Each phenomenon studied separately

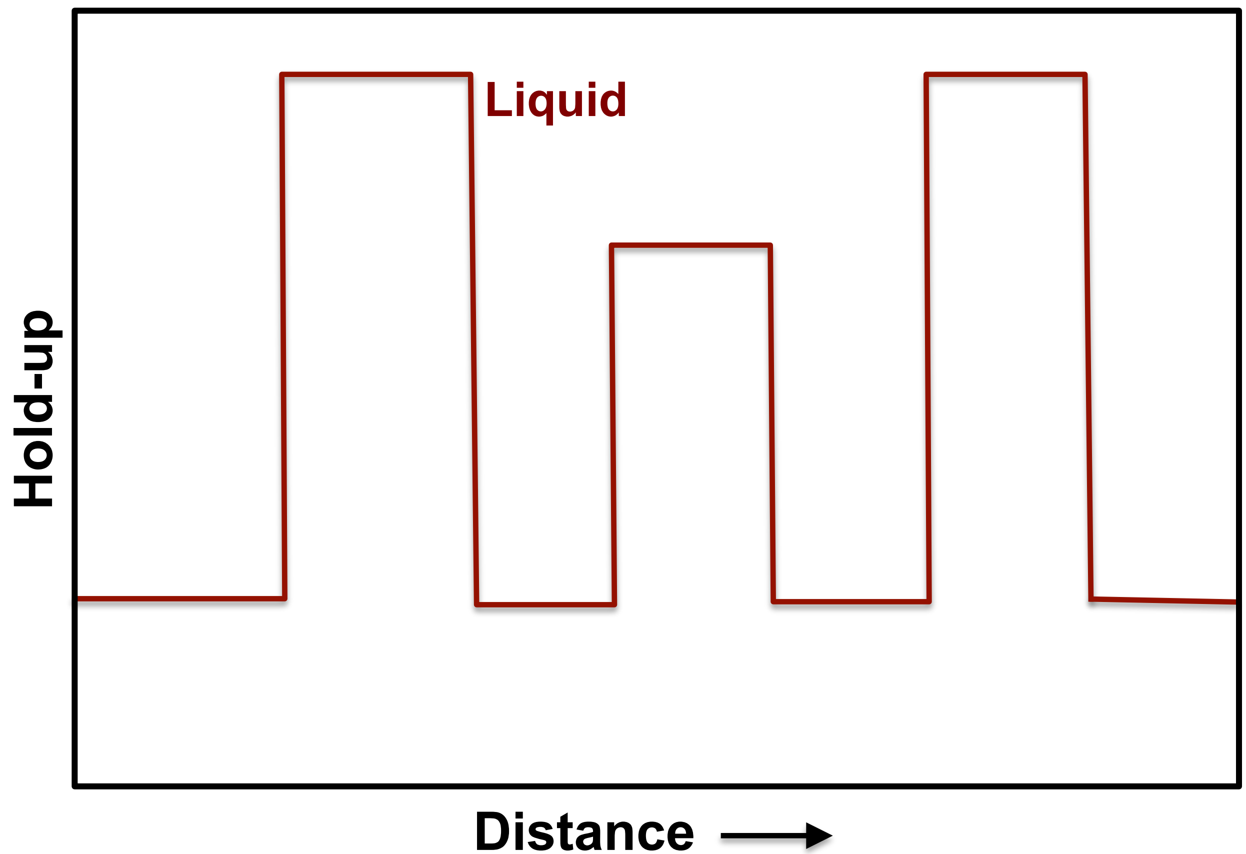
Multiphase flow & hydrate formation are interdependent

Multiphase Flow & Hydrate Interdependence



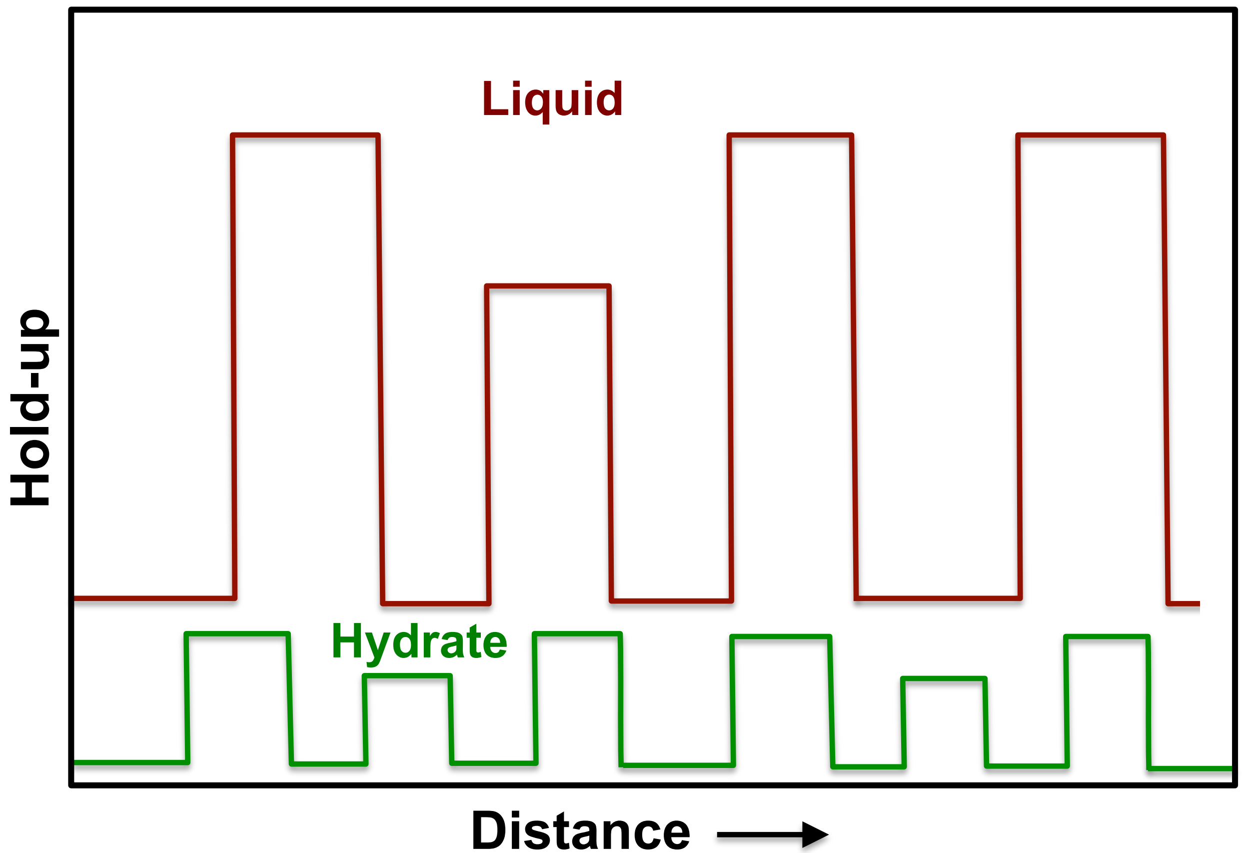
- Hydrate formation = f(LL, WC, mixture velocity, T, P)
- **CSMFlow:** incorporates flow regime in calculations
- Effort to understand multiphase flow and **its effect on hydrate formation (and vice-versa)**

Multiphase Flow & Hydrate Interdependence



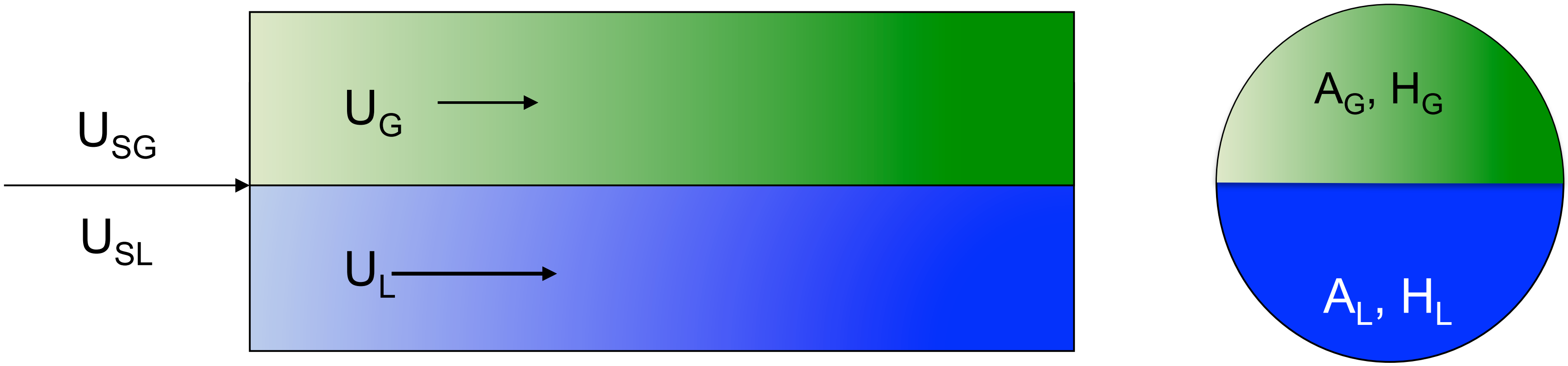
Flow characteristics: hold-up, slug length, slug frequency, ΔP

Multiphase Flow & Hydrate Interdependence



Flow characteristics: hold-up, slug length, slug frequency, ΔP

Fundamental Multiphase Flow Concepts



Hold-up:

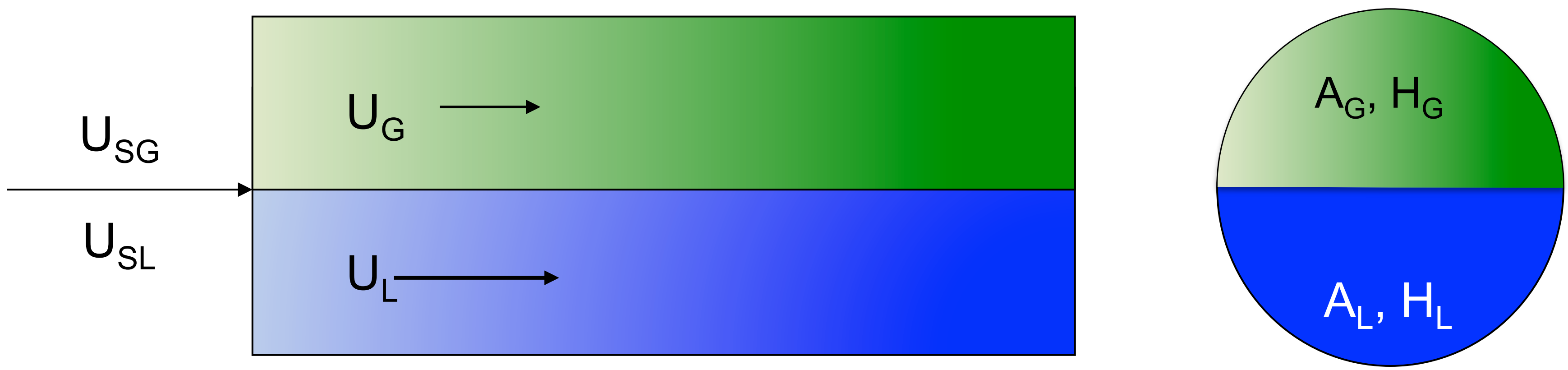
$$H_i = \frac{A_i}{A_{\text{pipe}}}$$

Superficial Velocity: $$U_{Si} = \frac{Q_i}{A_{\text{pipe}}}$$

Linear Velocity: $$U_i = \frac{U_{Si}}{H_i}$$

where 'i' stands for phase (L, G or Hyd)

Fundamental Multiphase Flow Concepts

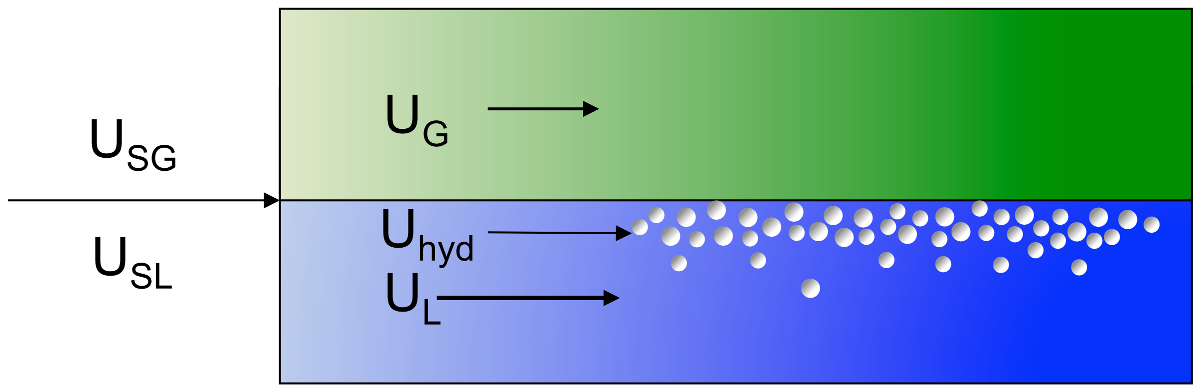


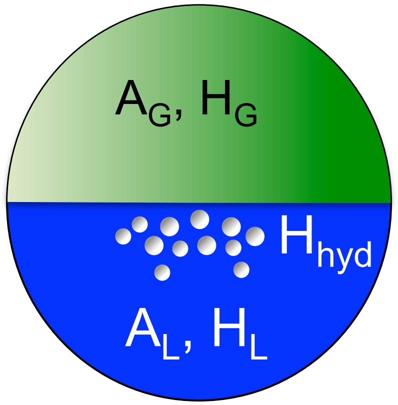
Phases hold-up: $H_G + H_L = 1$

Mixture velocity: $U_M = U_{SG} + U_{SL}$

Slip Velocity: $U_{S\ (G\text{-}L)} = U_G - U_L$

Fundamental Multiphase Flow Concepts





Phases hold-up: $H_G + H_L$ **$+ H_{hyd} = 1$**

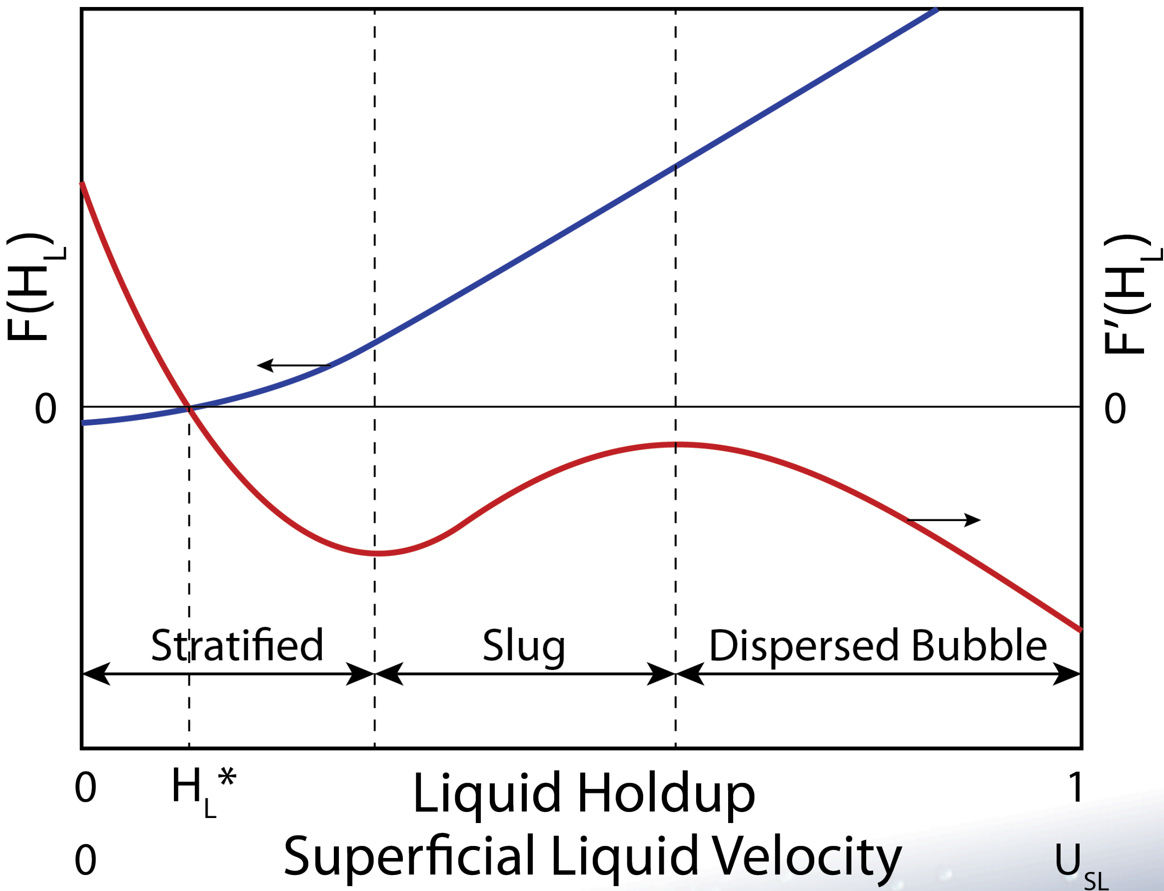
Mixture velocity: $U_M = U_{SG} + U_{SL}$ **$+ U_{Shyd}$**

Slip Velocity: $U_{S\ (G\text{-}L)} = U_G - U_L$

$U_{S\ (L\text{-}hyd)} = U_L - U_{hyd}$

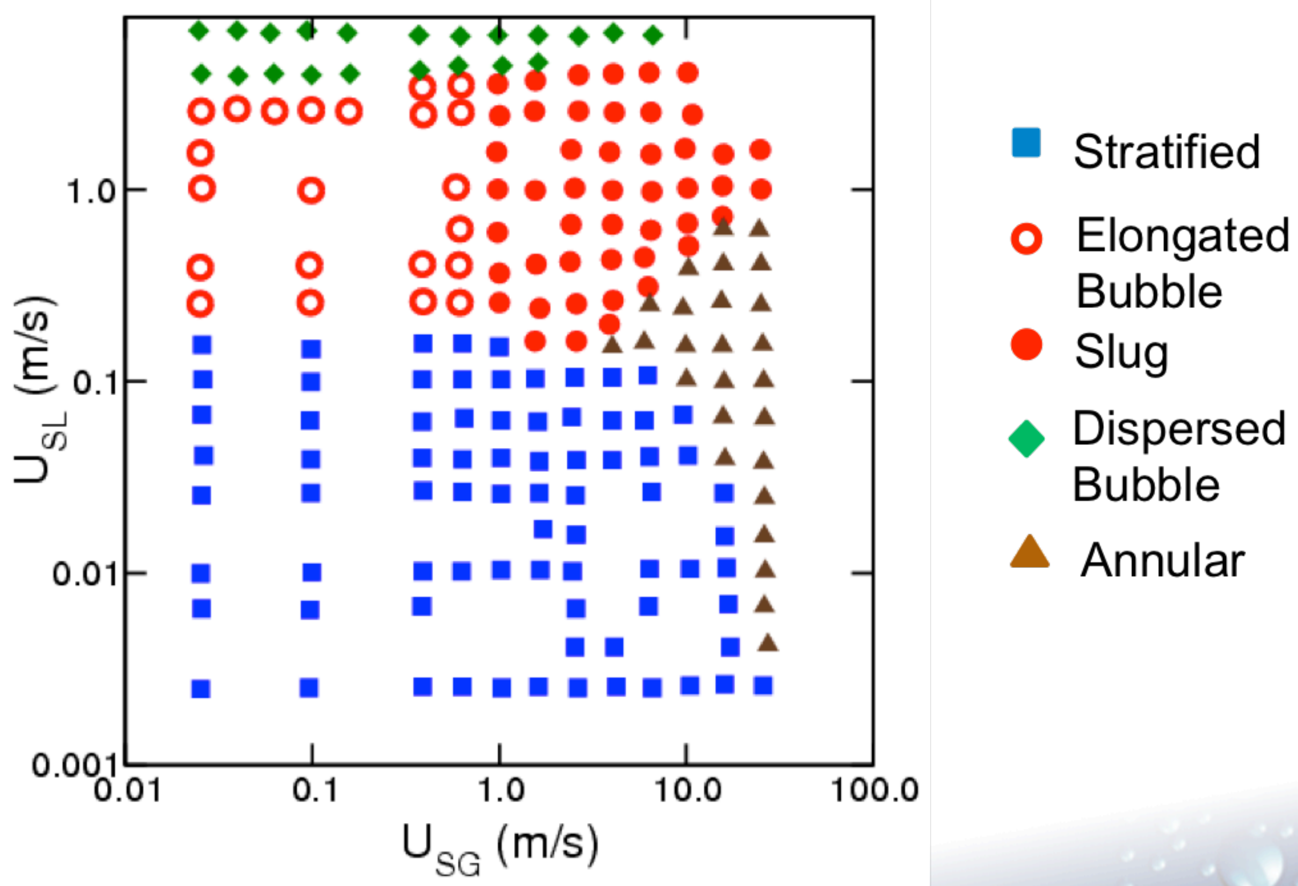
Determining Flow Regime and Transitions

$$F(H_L) = U_S H_L^2 + (U_M - U_S)H_L - U_{SL} \qquad F'(H_L) = U_S H_L^2 + (U'_M - U_S)H_L - U'_{SL}$$



CSMFlow: Unique Tool for Multiphase Flow

Air-Water system (Shoham, 1984)



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CSMFlow: Unique Tool for Multiphase Flow

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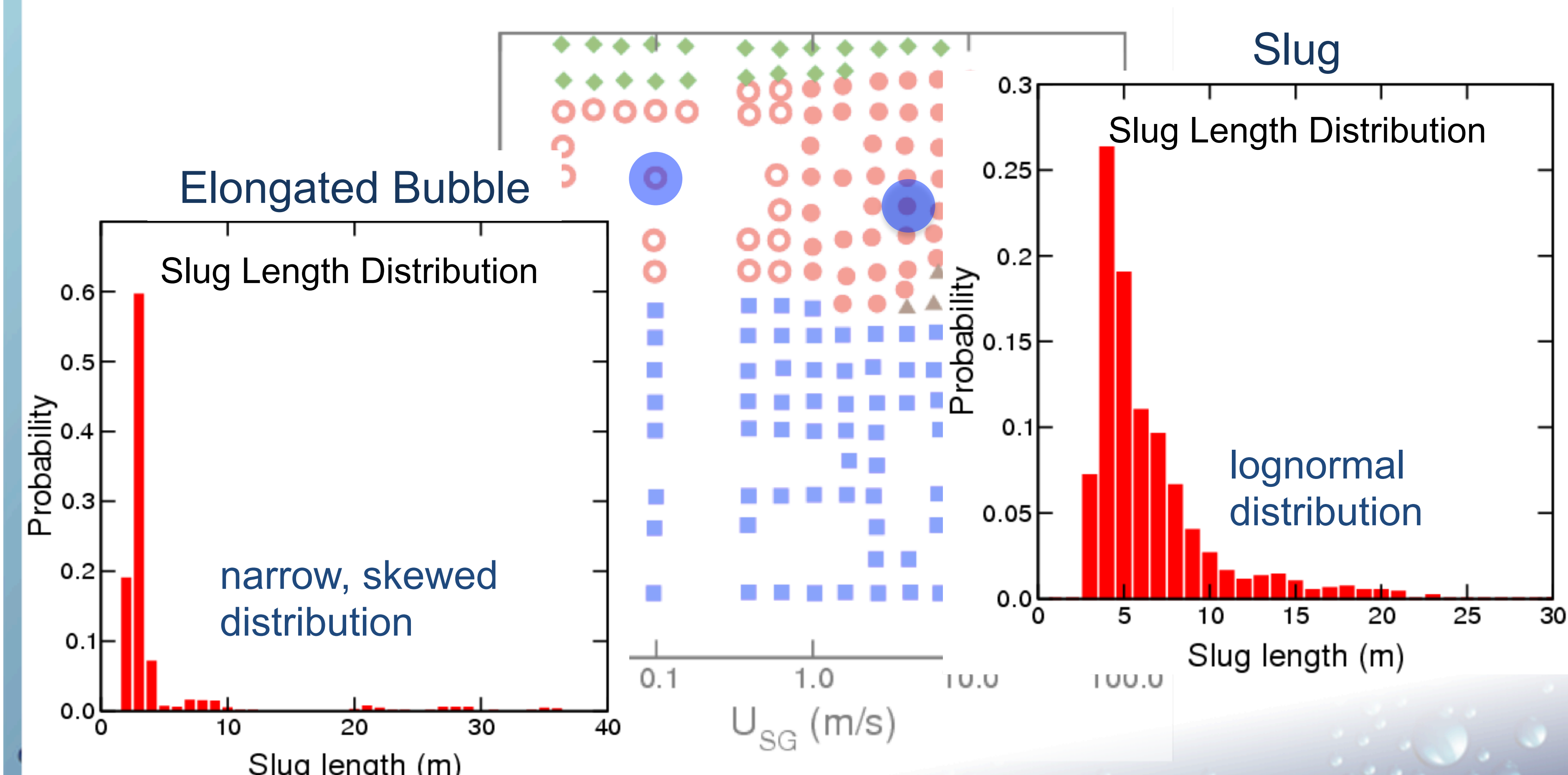
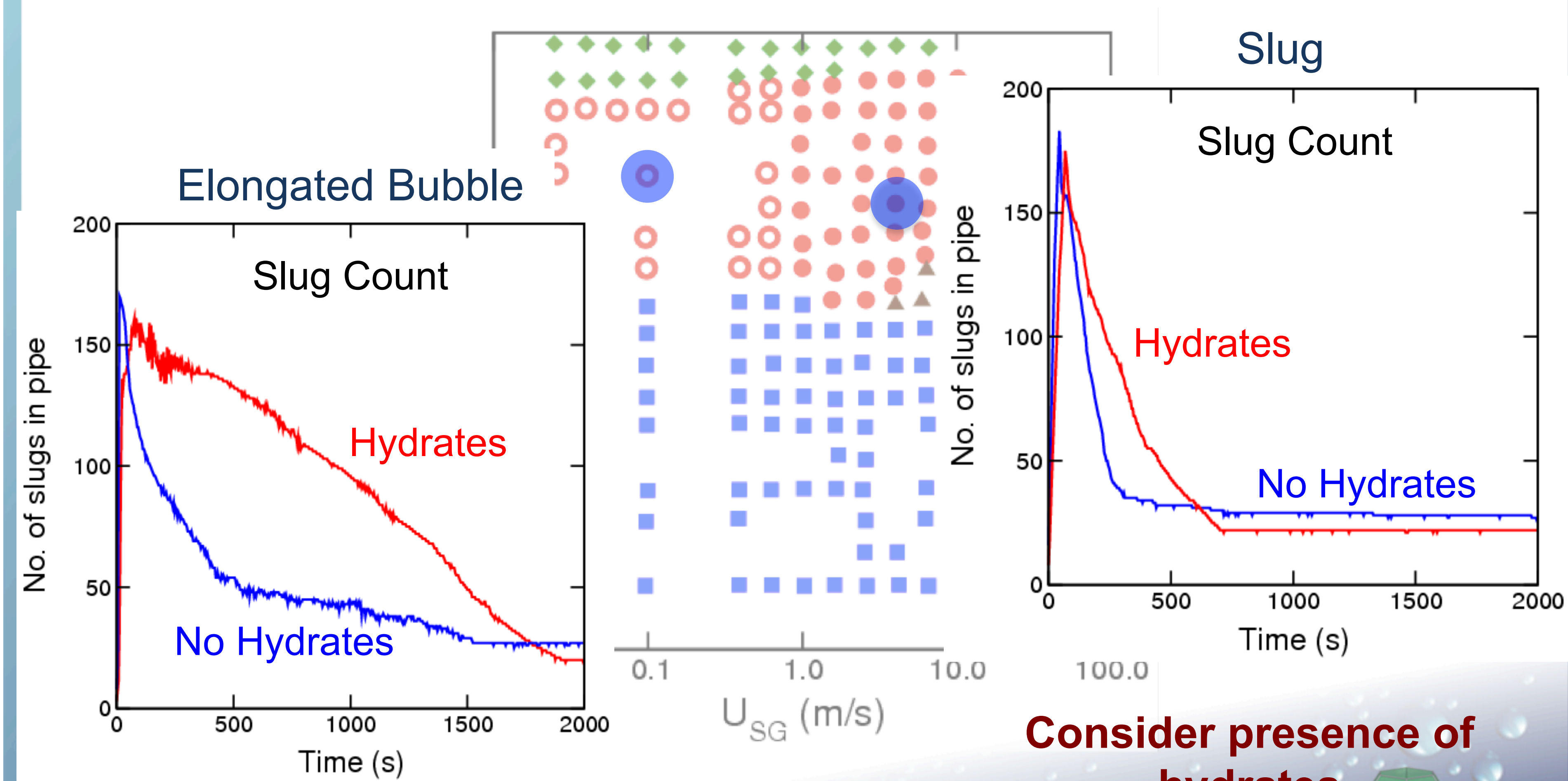


CSMFlow: Unique Tool for Multiphase Flow

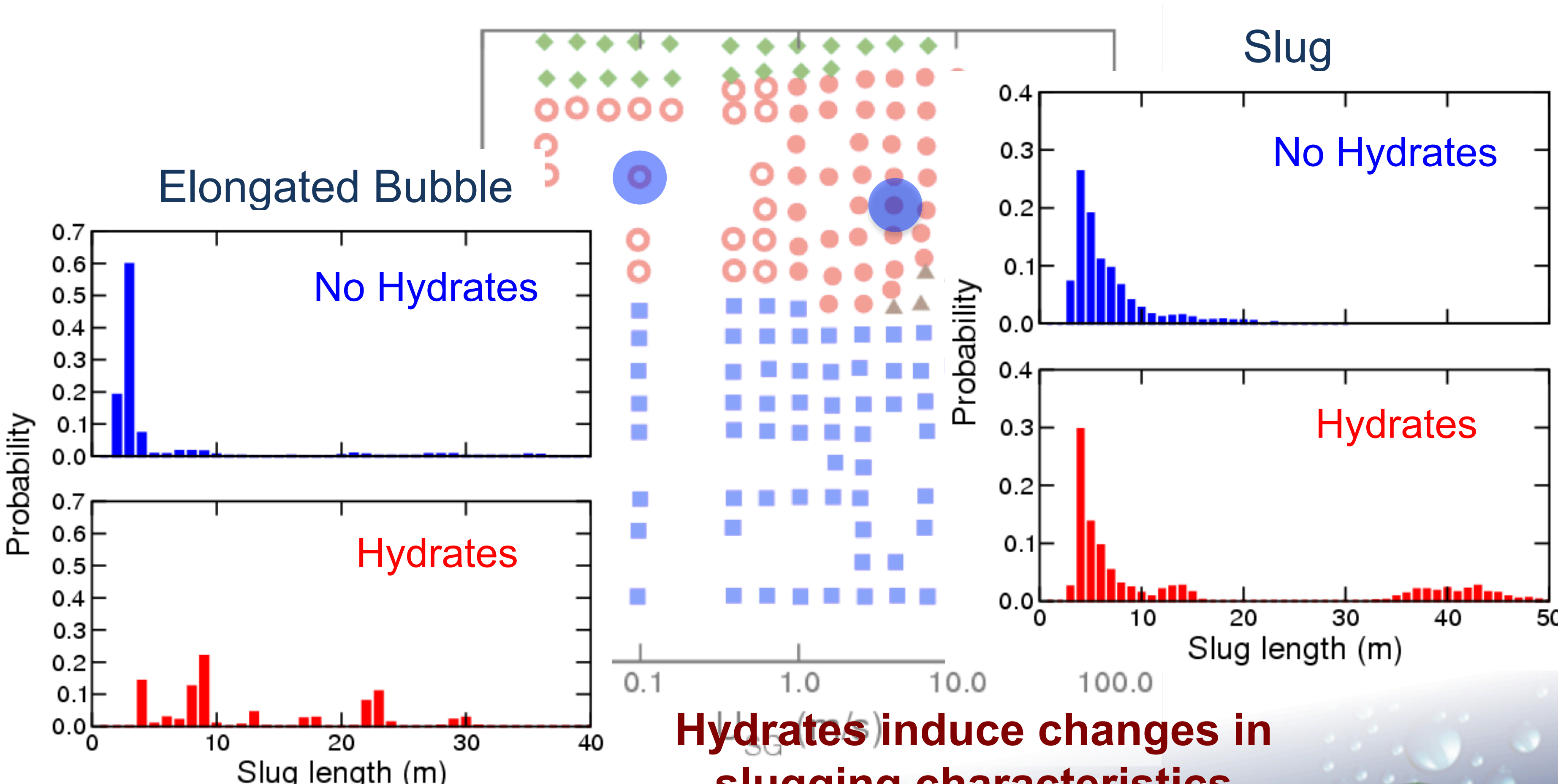
Air-Water system (Shoham, 1984)



Consider presence of hydrates

CSMFlow: Unique Tool for Multiphase Flow

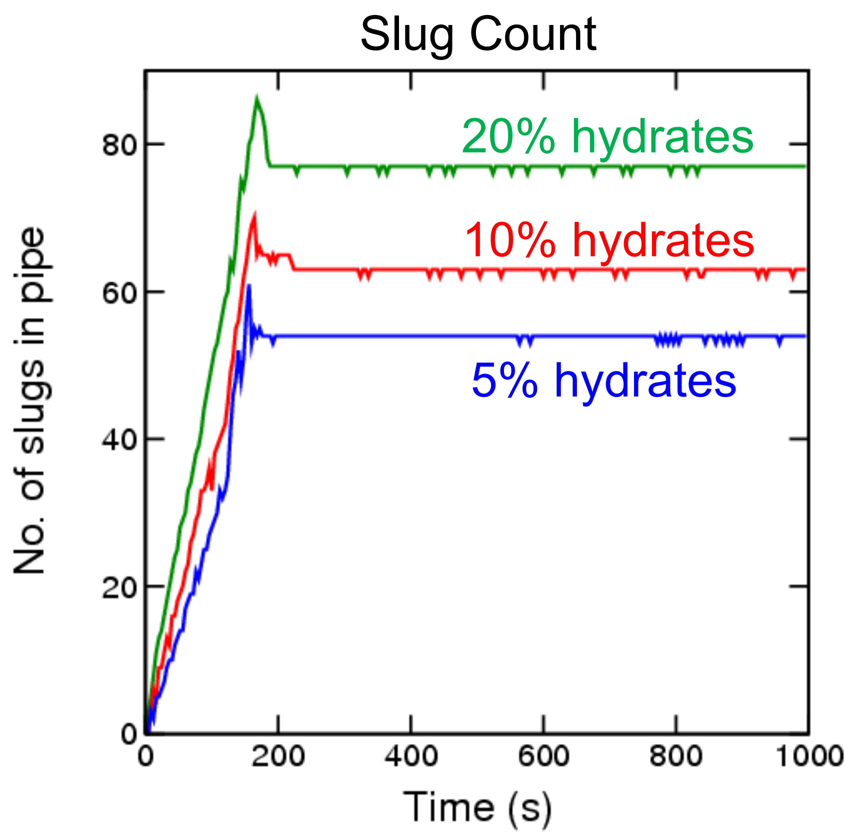
Air-Water system (Shoham, 1984)

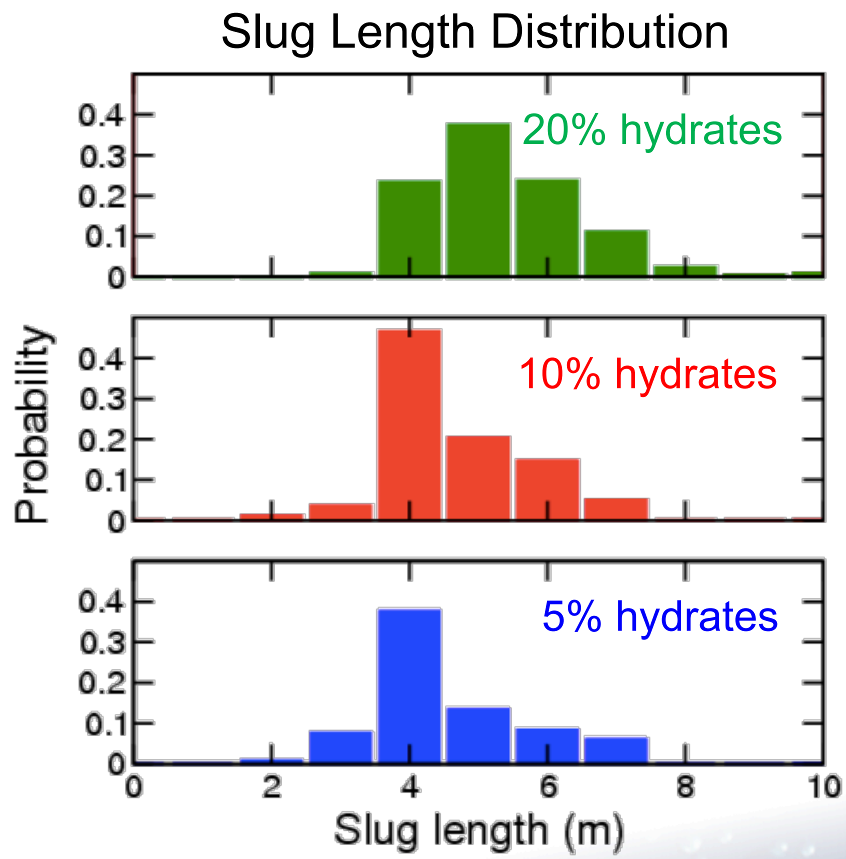


Hydrates induce changes in slugging characteristics

CSMFlow: Unique Tool for Multiphase Flow

Hydrate Fraction Plays Important Role in Flow Behavior





Can we infer hydrate formation from slugging characteristics?

Summary

- **Hydrate avoidance works!** Past, Present and Future
- Hydrate management: **live with hydrates**
- Must know the **risk of hydrate** formation and plugging
- More challenging production conditions: **much to learn about hydrates**

THANK YOU!

Questions???

Contact: asum@mines.edu