



ACADEMIC SEMINAR

Gas hydrate formation and transport at high water-cut systems in the presence of salts and additives

Hanoi, 05-2024

Outlines



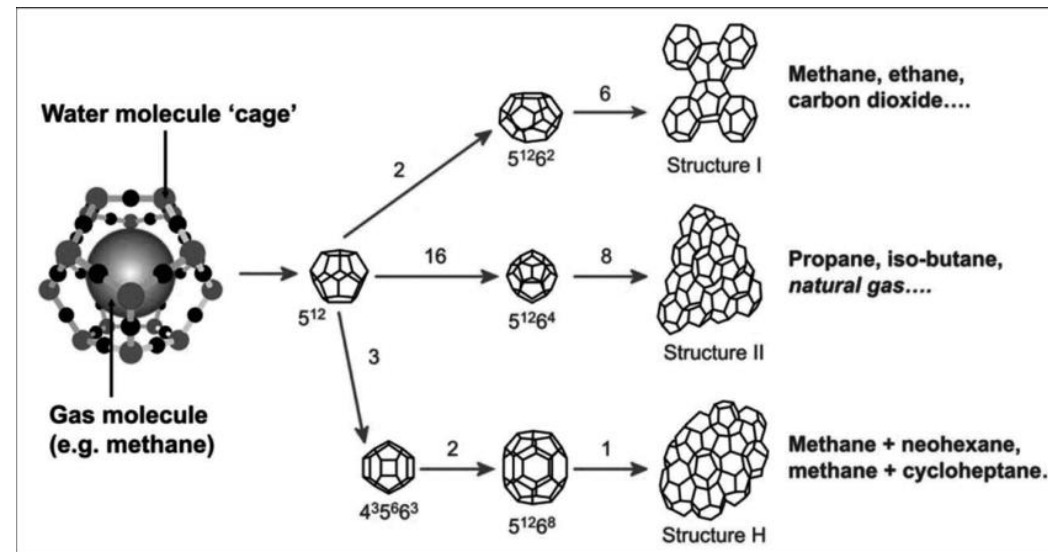
1. Hydrate backgrounds and applications
2. Gas hydrates in flow assurance
3. Experimental Methodology
4. Results & Discussion
5. Conclusions & Perspectives

1. Hydrate backgrounds and applications

- Hydrate is a solid compound formed by water and guest molecule (hydrocarbons, H_2S , CO_2 , H_2 , N_2 , O_2 , etc.) at low temperature and possibly at high pressure.
- Applications of hydrates: methane hydrate resource as a huge future fuel, gas storage and separation, water treatment, flow assurance, etc.



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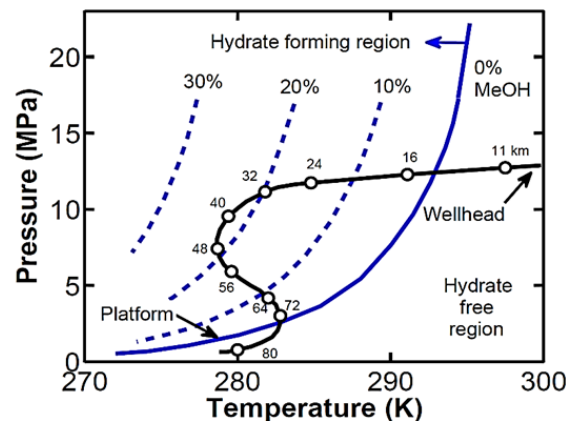


Hydrate structures (from Center for Gas Hydrate Research – Heriot Watt)

2. Gas hydrates in flow assurance



- Methane hydrate formed by water and gas at 4°C and 80 bar.
- Methane hydrate can cause plugs in oil pipelines (costly to prevent, remove and induce safety risks).
- Oil and gas fields gradually become mature, leading to an increase in water production (or high water cut).
- Anti-Agglomerant-Low Dosage Hydrate Inhibitors (AA-LDHIs) are the best candidates to prevent **PLUG** compared to Thermodynamic Inhibitors (THIs) and Kinetic Hydrate Inhibitors (KHIs).



(Sloan and Koh, 2008)



(Subsea pipelines - Oilstates, 2017)

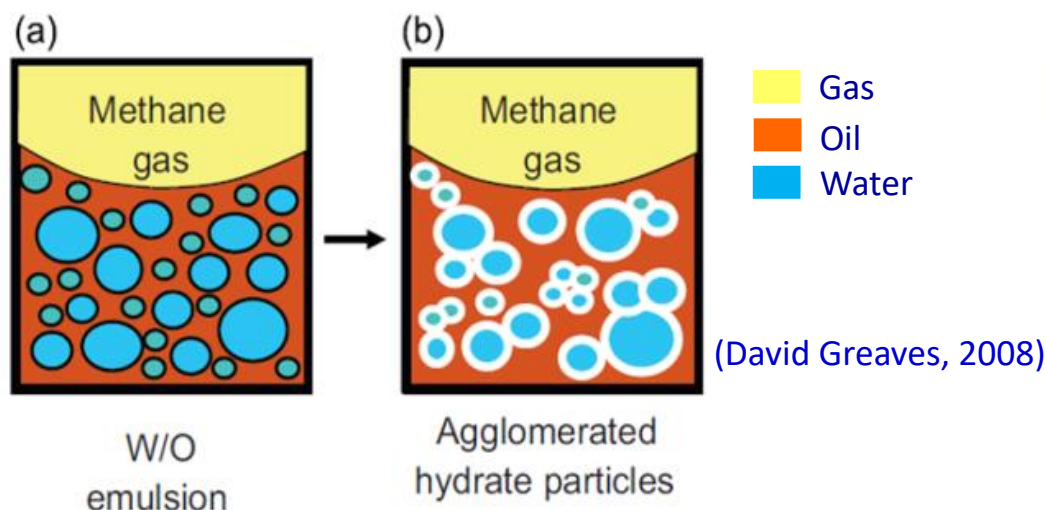


(Hydrate recovered at slug catcher-Petrobras)

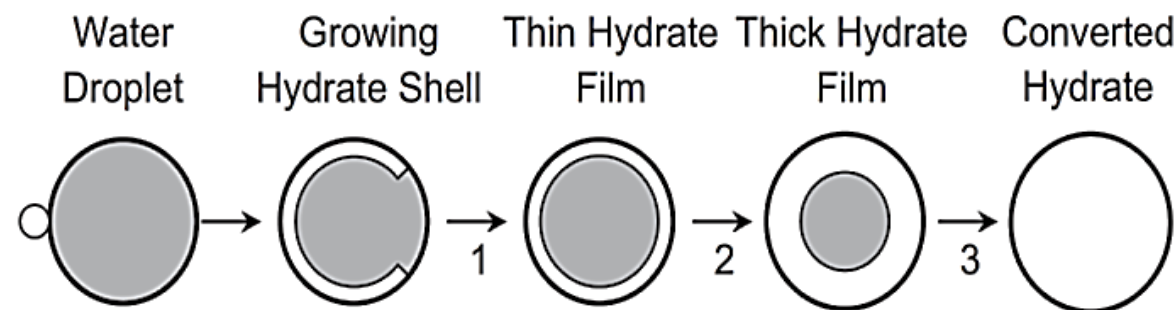
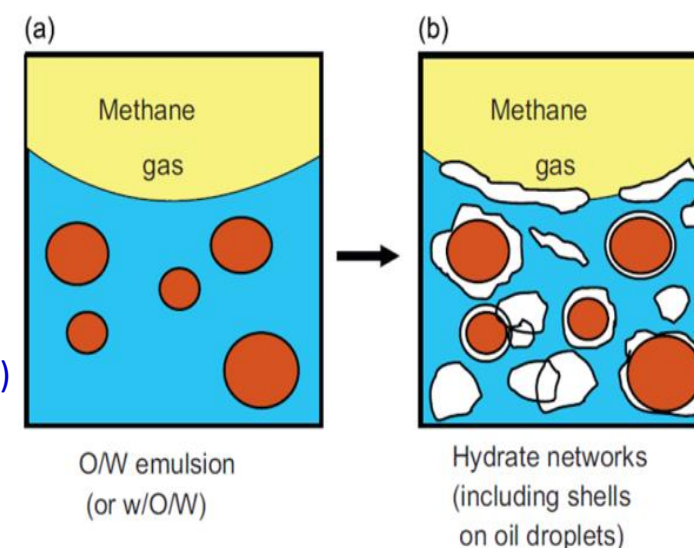
2. Gas hydrates in flow assurance

2.1. Gas hydrate formation in emulsion

At low water cut (W/O emulsion)



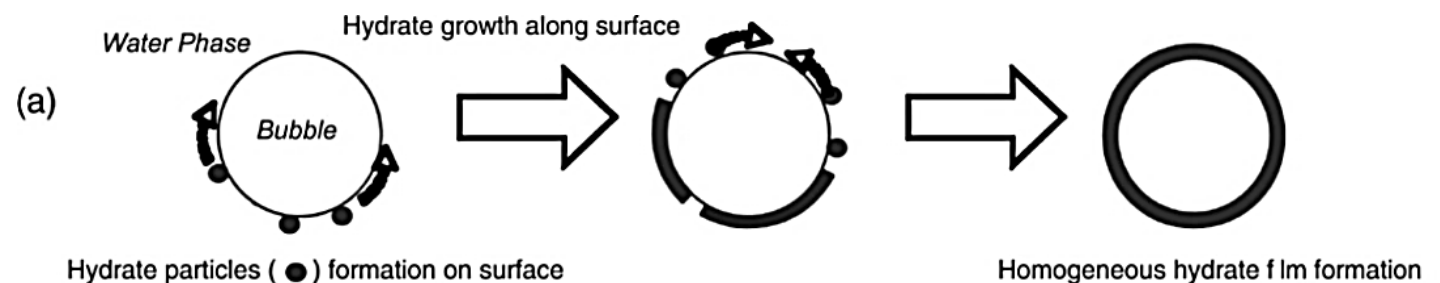
At high water cut (O/W emulsion)



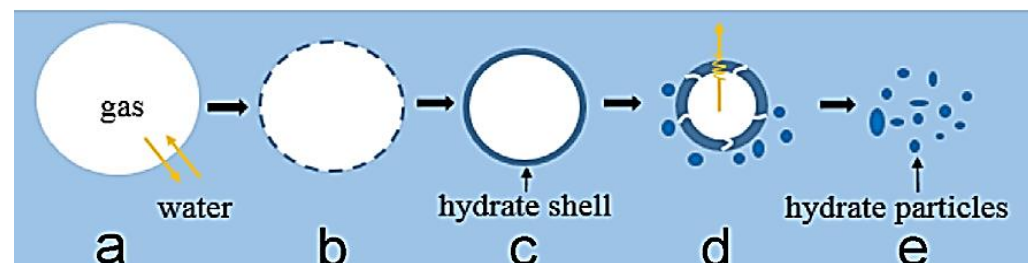
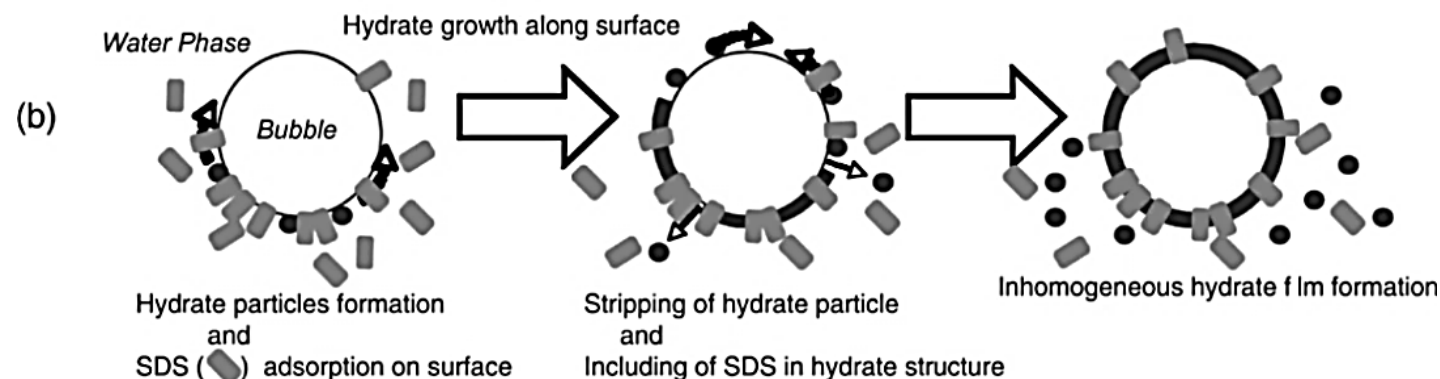
(Taylor, 2007)

2. Gas hydrates in flow assurance

2.2. Hydrate formation around gas bubble



(Tajima, 2010)



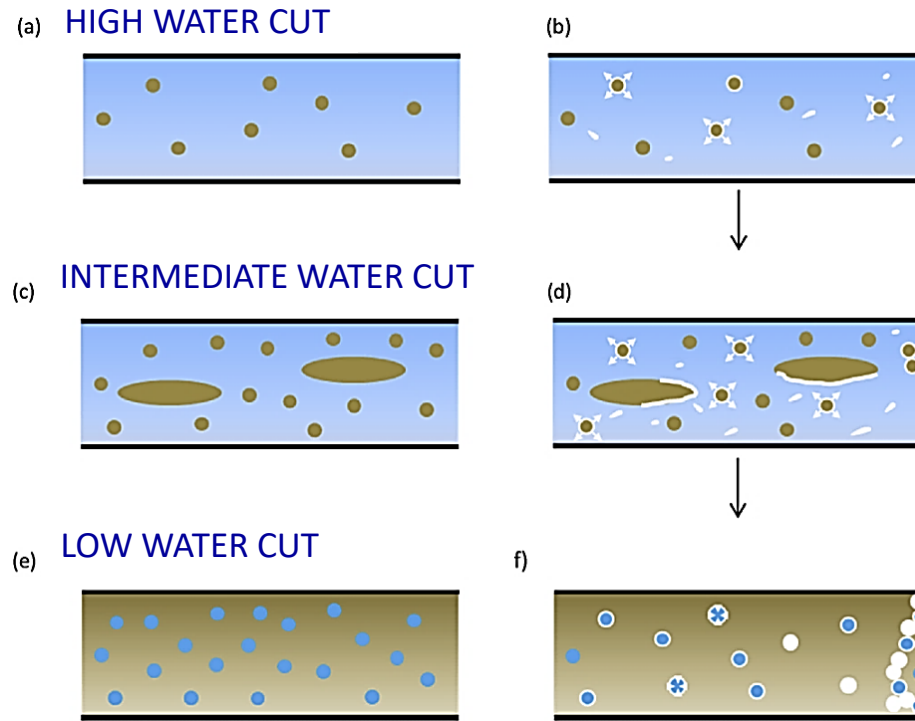
(C. Li & Huang, 2016)

2. Gas hydrates in flow assurance

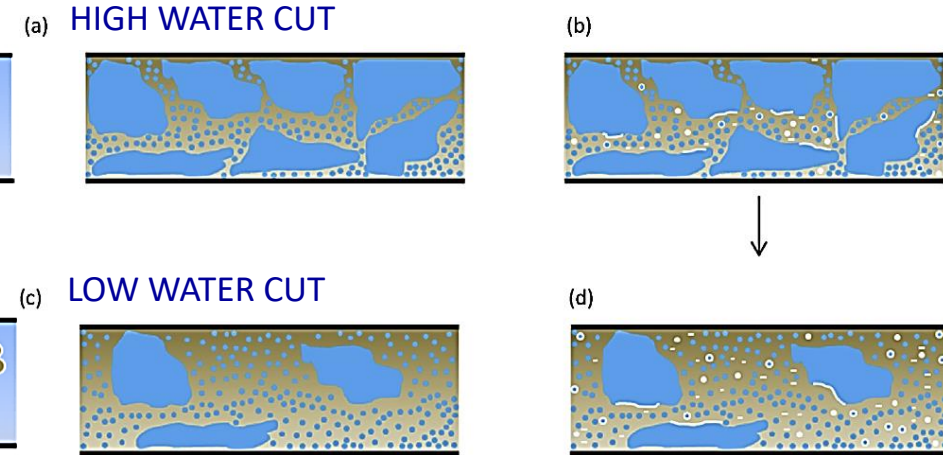
2.3. Multi-phase hydrate slurry flow



Crystallization under flowing without AA-LDHI



Crystallization under flowing with AA-LDHI

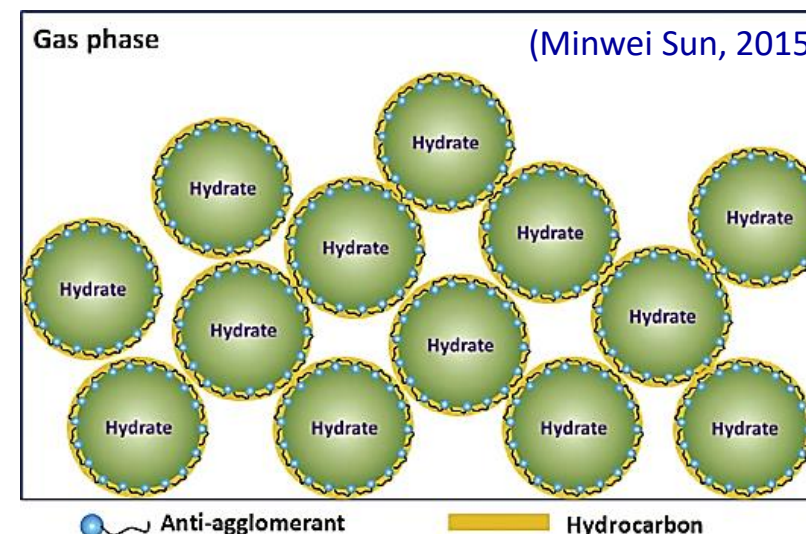
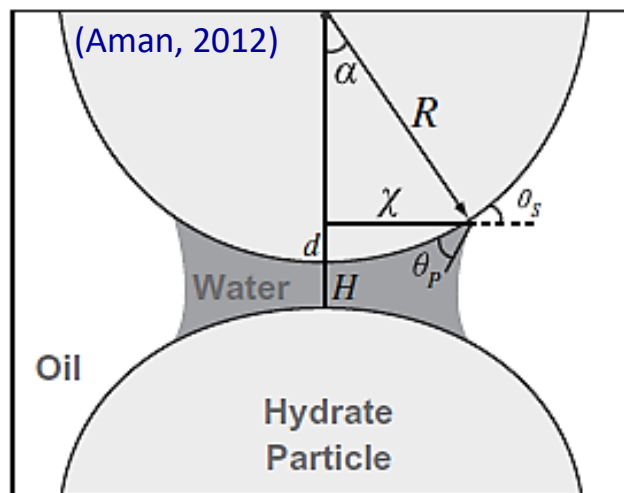


(Melchuna, 2016)

2. Gas hydrates in flow assurance

2.4. Agglomeration and Anti-Agglomeration

- ❑ Agglomeration is mainly attributed to capillary forces (Israelachvili, 1991; Austvik et al., 2000; Aspenes et al., 2010).
- ❑ AA-LDHI are surfactants which reduce particle adhesion.



- ❑ An effective AA-LDHI should (Anklam, 2008):
 - Reduce the size of hydrate particles
 - Decrease the interfacial tension between water and oil phase
 - Change the wettability of hydrate surface to oil-wet

Experimental data were recorded online by LABVIEW, PVM, and FBRM software

PVM

FBRM

Gas-Lift

Moineau Pump

CH₄

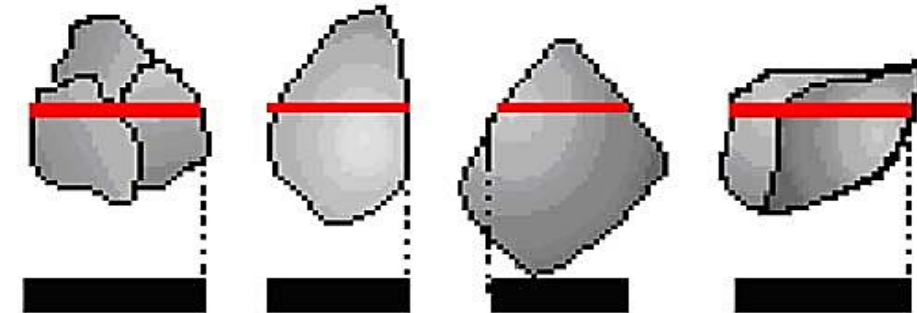
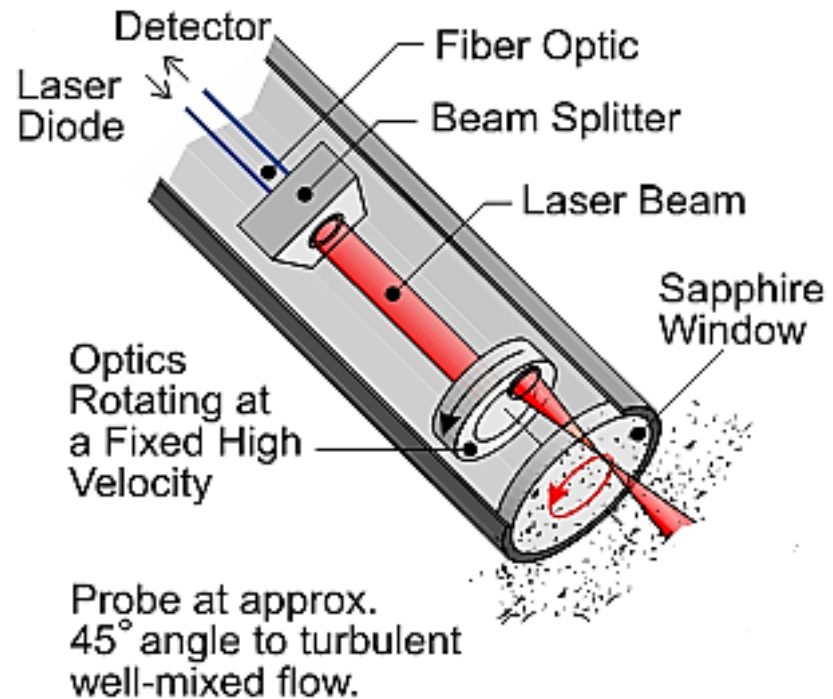
12m



3. Experimental Methodology



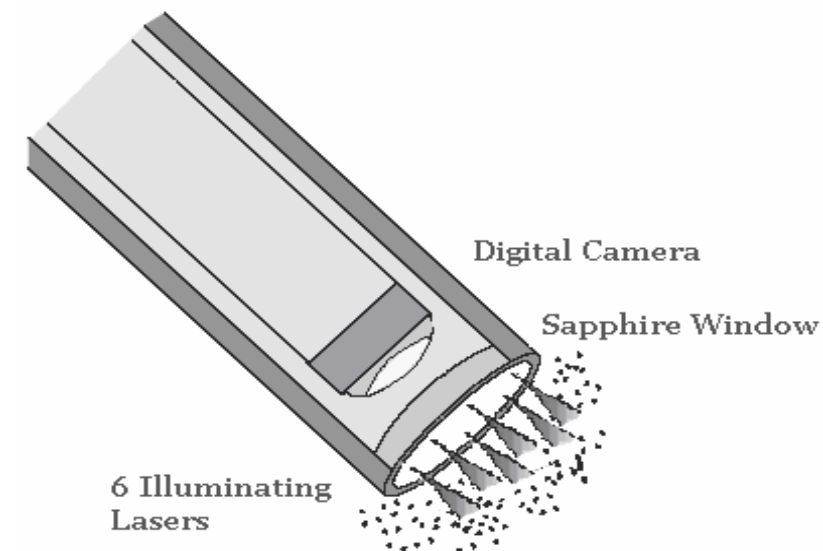
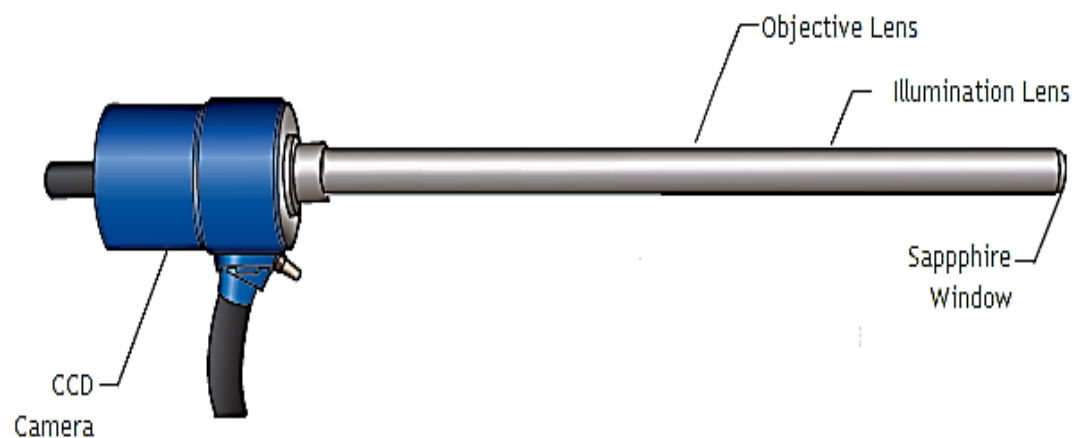
- FBRM



The principle of FBRM probe measurement
(Mettler-Toledo, 2007)

3. Experimental Methodology

- PVM



The principle of PVM probe measurement
(PVM, 2009)

4. Results & Discussion

In preparation to
publish soon...

Table 1. Summary of hydrate slurry transport phenomena in high water cut systems.

| | Pressure Drop and Flowing | Experiments | Phenomena in Hydrate Transport | Average Crystallization Rate - $\bar{R}(t)$ | HV |
|------------------------------------|--|--|---|---|-----------------|
| | - | - | - | (%HV.min ⁻¹) | (%) |
| Heterogeneous with plug | High pressure drop in the horizontal line and stop flowing | ≤0.5%AA-LDHI at 150-400L.h ⁻¹ at 85-90%LV | Agglomeration and Deposition | Low- Intermediate | 8.65- 26.78 |
| | | 1%AA-LDHI at 150L.h ⁻¹ | Agglomeration and Deposition | Intermediate | 17.49- 24.02 |
| | | NaCl-400L.h ⁻¹ and 80%WC-NaCl- 150L.h ⁻¹ | Agglomeration and Deposition | Low- Intermediate | 9.12- 24.12 |
| Heterogeneous No plug | High pressure drop in the horizontal line and flowing | ≥1%AA-LDHI at 400L.h ⁻¹ | Agglomeration and Deposition | Intermediate - High | 22.53- 26.90 |
| | | NaCl and ≥0.5AA- LDHI at 400L.h ⁻¹ | Less Agglomeration and Less Deposition | Intermediate | 34.41- 43.58 |
| Homogeneous No plug | Low pressure drop and flowing | 100%LV and ≤0.05%AA-LDHI | Agglomeration | Low | 1.74- 5.23 |
| | | 100%WC with NaCl at 150L.h ⁻¹ | Agglomeration and Deposition | Low | 6.10- 7.69 |
| | | NaCl and ≥0.5AA- LDHI at 150L.h ⁻¹ | Less Agglomeration and Less Deposition | Intermediate | 29.27- 50.82 |

Hydrate slurry
transport
phenomena in high
water cut systems

4. Results & Discussion

In preparation to
publish soon...

Stability of liquid-
liquid dispersion
once hydrate
formation

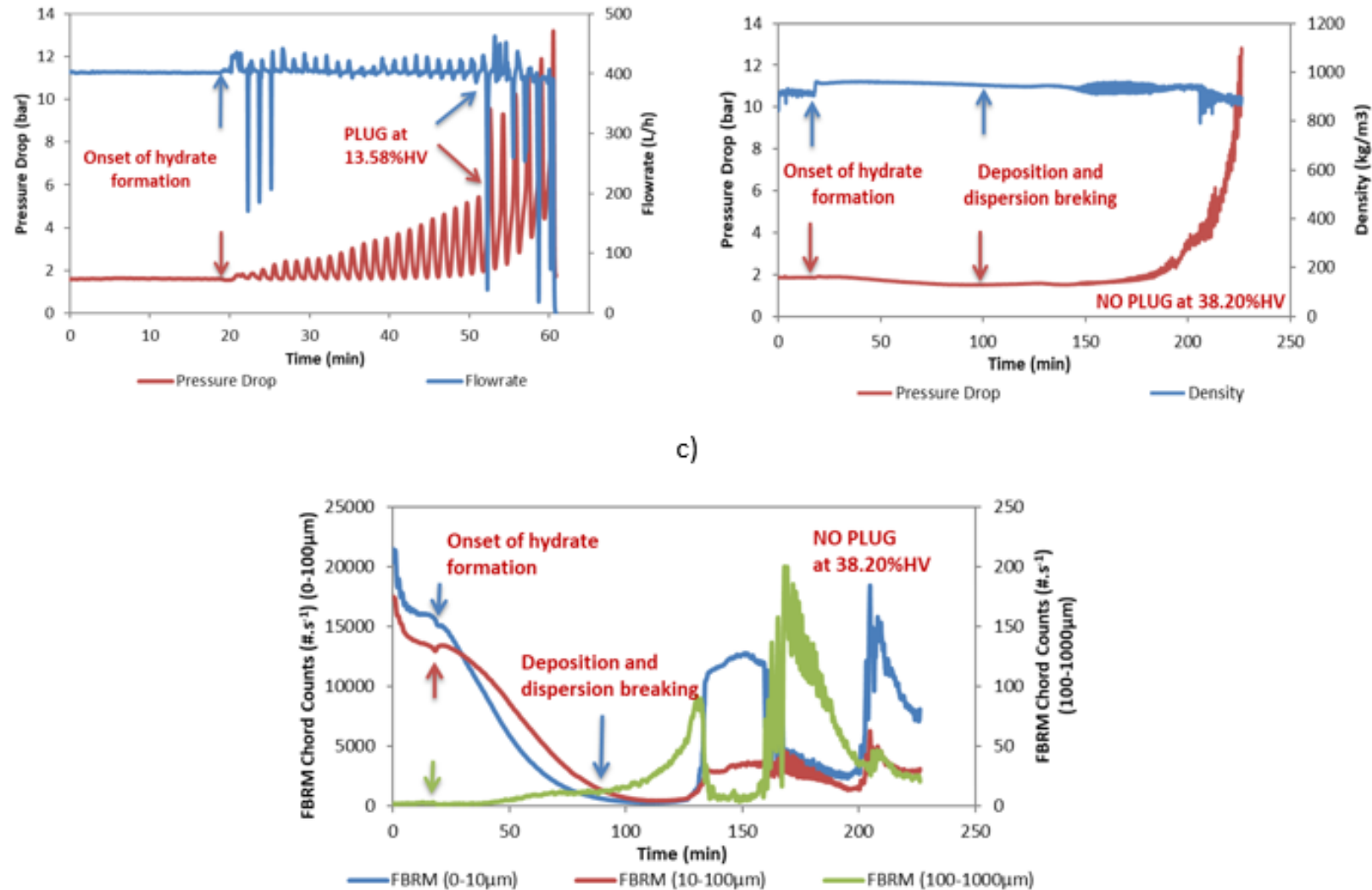
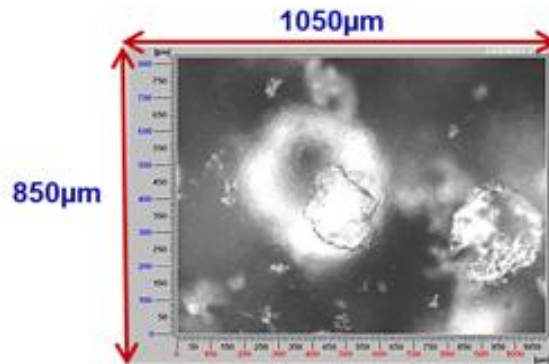
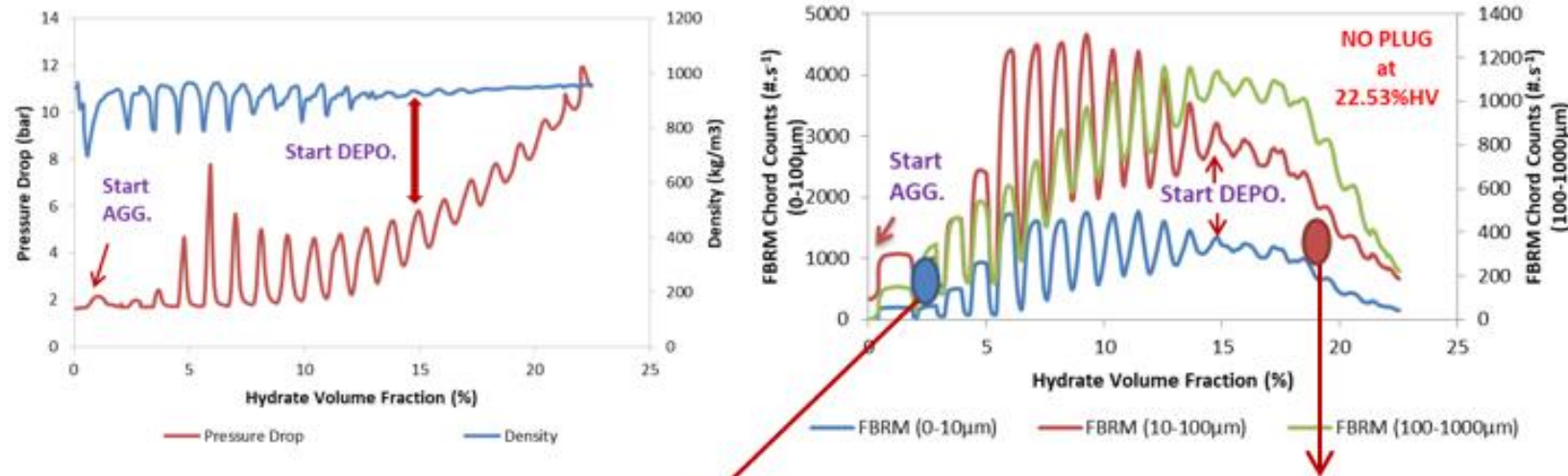


Fig. 4. Effect of hydrate formation on flowing and stability of liquid-liquid dispersion: (a) pressure drop and flowrate versus time in the experiment of 80%WC-NaCl-85%LV-75bar-400L.h⁻¹; (b, c) pressure drop, density and FBRM chord counts versus time in the experiment of 80%WC-NaCl-1%AA-LDHI-85%LV-75bar-400L.h⁻¹.

4. Results & Discussion

In preparation to
publish soon...

Quick and slow
(agglomeration
and deposition)
heterogeneity of
hydrate slurry flow



**QUICK
HETEROGENEITY**
 $\bar{R}(t)=0.81\%HV/min$

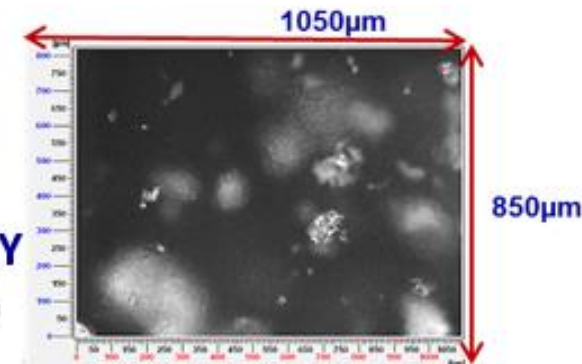


Fig. 5. Quick heterogeneity of hydrate slurry flow (pressure drop, density, FBRM chord counts and PVM images versus hydrate volume fraction in the experiment of 100%WC-1%AA-LDHI-85%LV-75bar-400L.h⁻¹).

**In preparation to
publish soon...**

FBRM Chord Counts (#.s⁻¹) (0-1000μm)

Pressure Drop (bar)/Density (kg/m³)

Hydrate Volume Fraction (%)

Legend:

- FBRM (0-10μm)
- FBRM (10-100μm)
- FBRM (100-1000μm)
- Pressure Drop x 10⁻²

Annotations:

- Start AGG. and DEPO.
- PLUG at 24.12%HV

Microscopy Images:

- Width: 1050μm
- Height: 850μm
- SLOW HETEROGENEITY**
- $\bar{R}(t) = 0.08\% \text{HV/min}$

15

4. Results & Discussion

In preparation to
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Quick and slow
(agglomeration
and deposition)
heterogeneity of
hydrate slurry flow

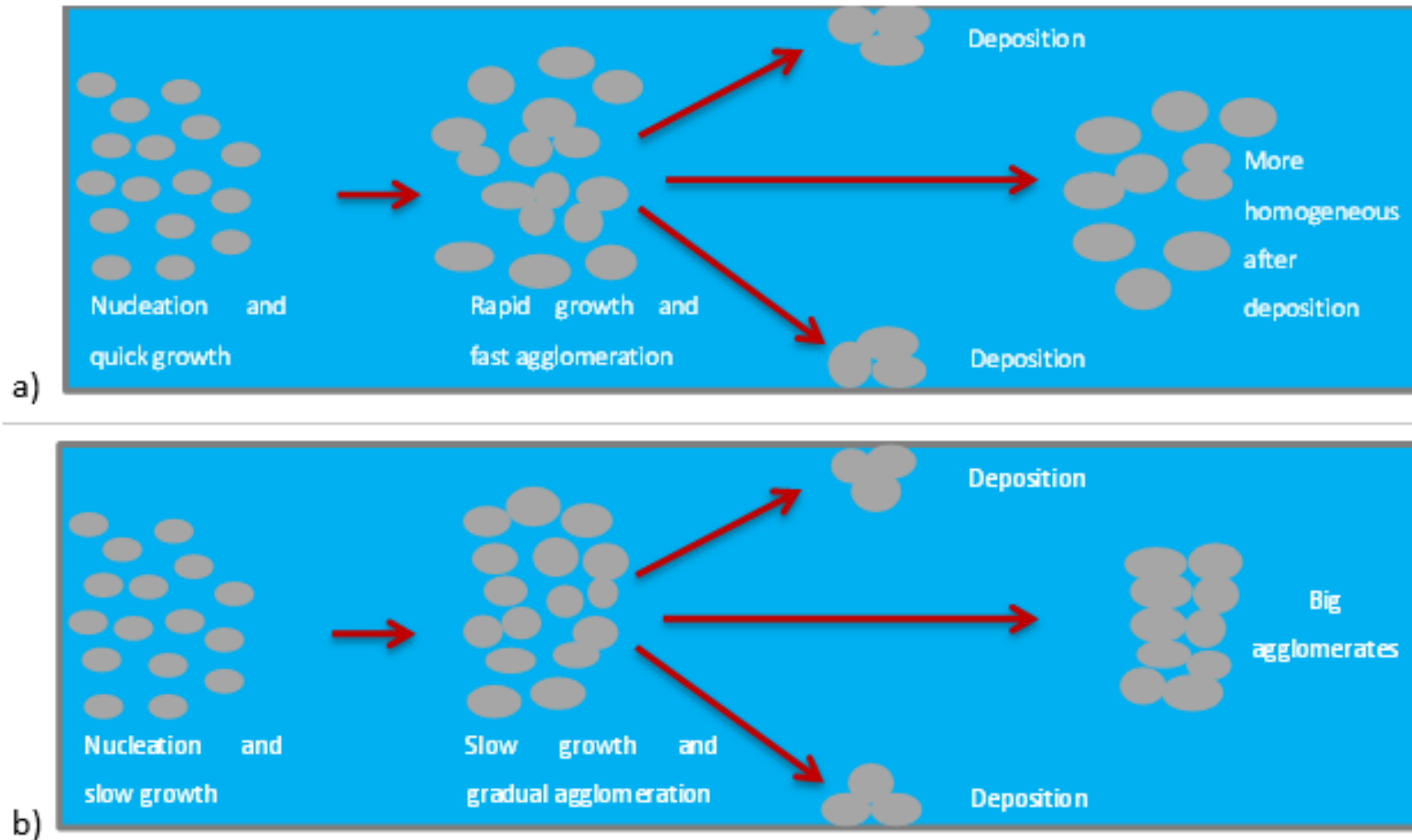


Fig. 7. Mechanism of quick (a) and slow (b) heterogeneity of hydrate slurry.

4. Results & Discussion

In preparation to
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Effect of flowrate

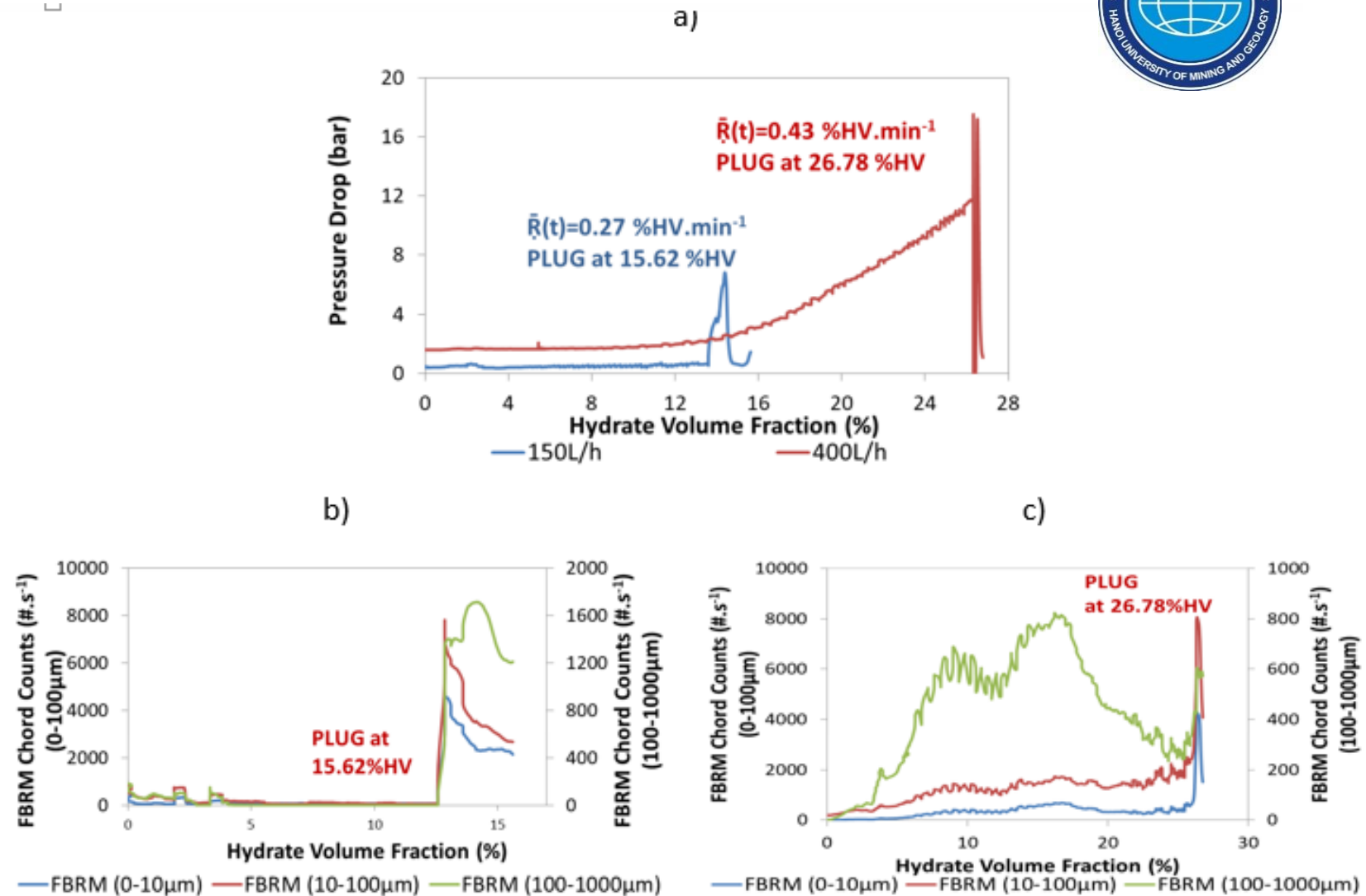


Fig. 8. Effect of flowrate on hydrate slurry transport: (a) pressure drop; (b,c) FBRM chord counts at 150 and 400L.h⁻¹ versus hydrate volume fraction in the experiments of 100%WC-0.5%AA-LDHI-85%LV-75bar at 150 and 400L.h⁻¹.

4. Results & Discussion

In preparation to
publish soon...

Effect of flowrate

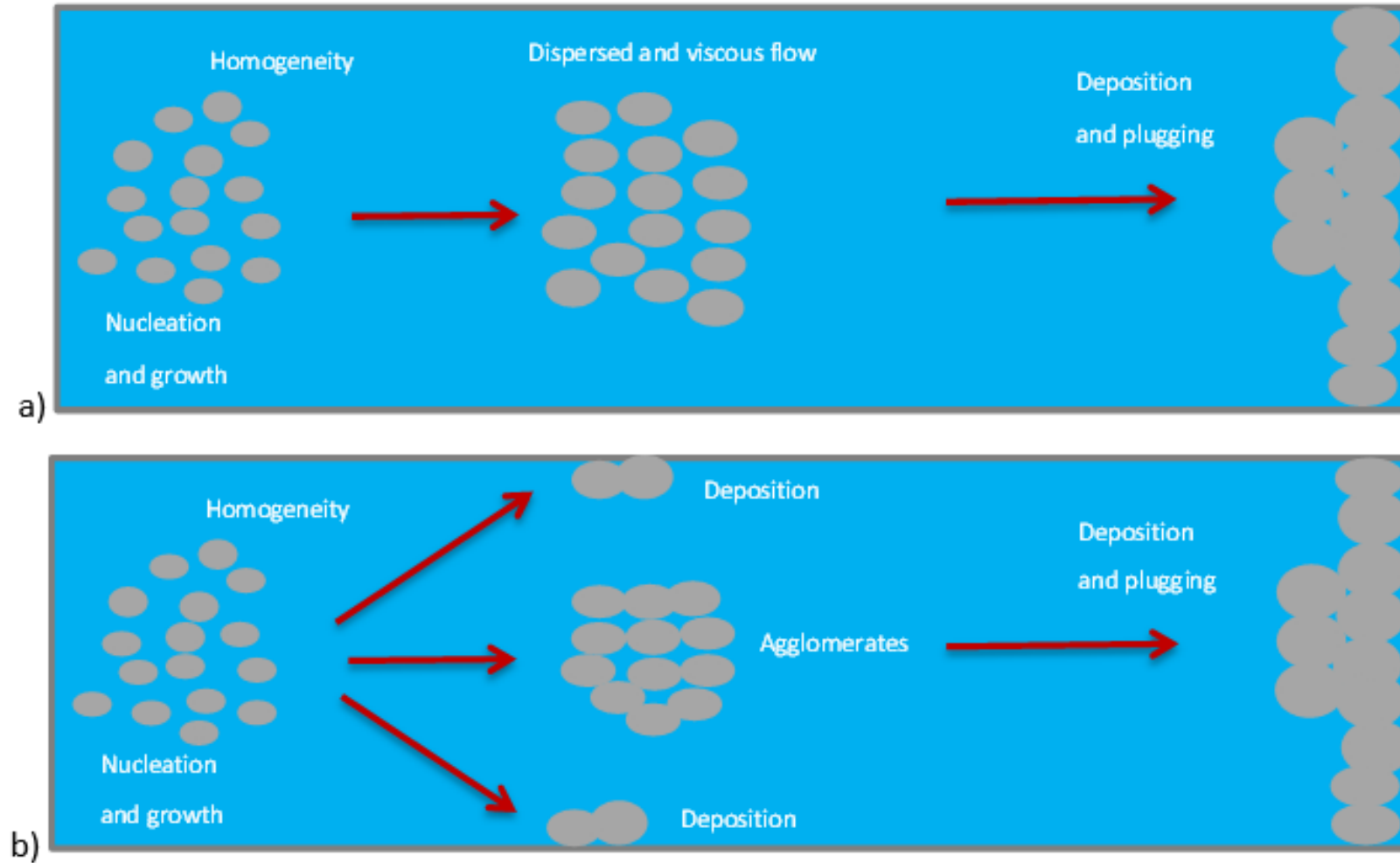


Fig. 9. Mechanism of hydrate slurry plugging at low (a) and high (b) flowrates.

4. Results & Discussion

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Effect of additive

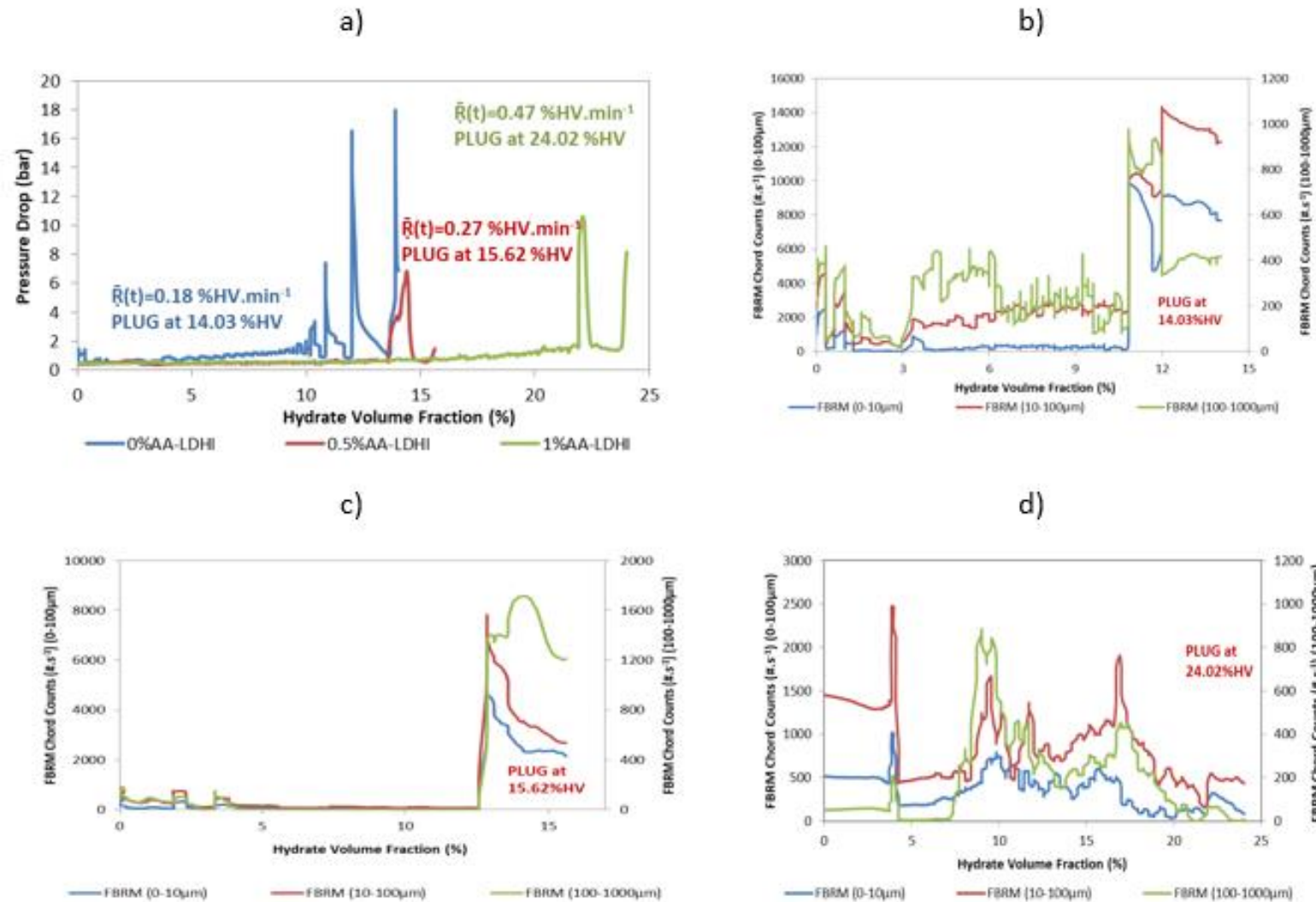


Fig. 10. Effect of additive on hydrate slurry transport: (a) pressure drop; (b,c,d) FBRM chord counts at 0-0.5-1%AA-LDHI versus hydrate volume fraction in the experiments of 100%WC-0-0.5-1%AA-LDHI-85%LV-75bar-150L.h⁻¹.

4. Results & Discussion

In preparation to
publish soon...

Effect of
combination of salt
and additive on
hydrate
transportability

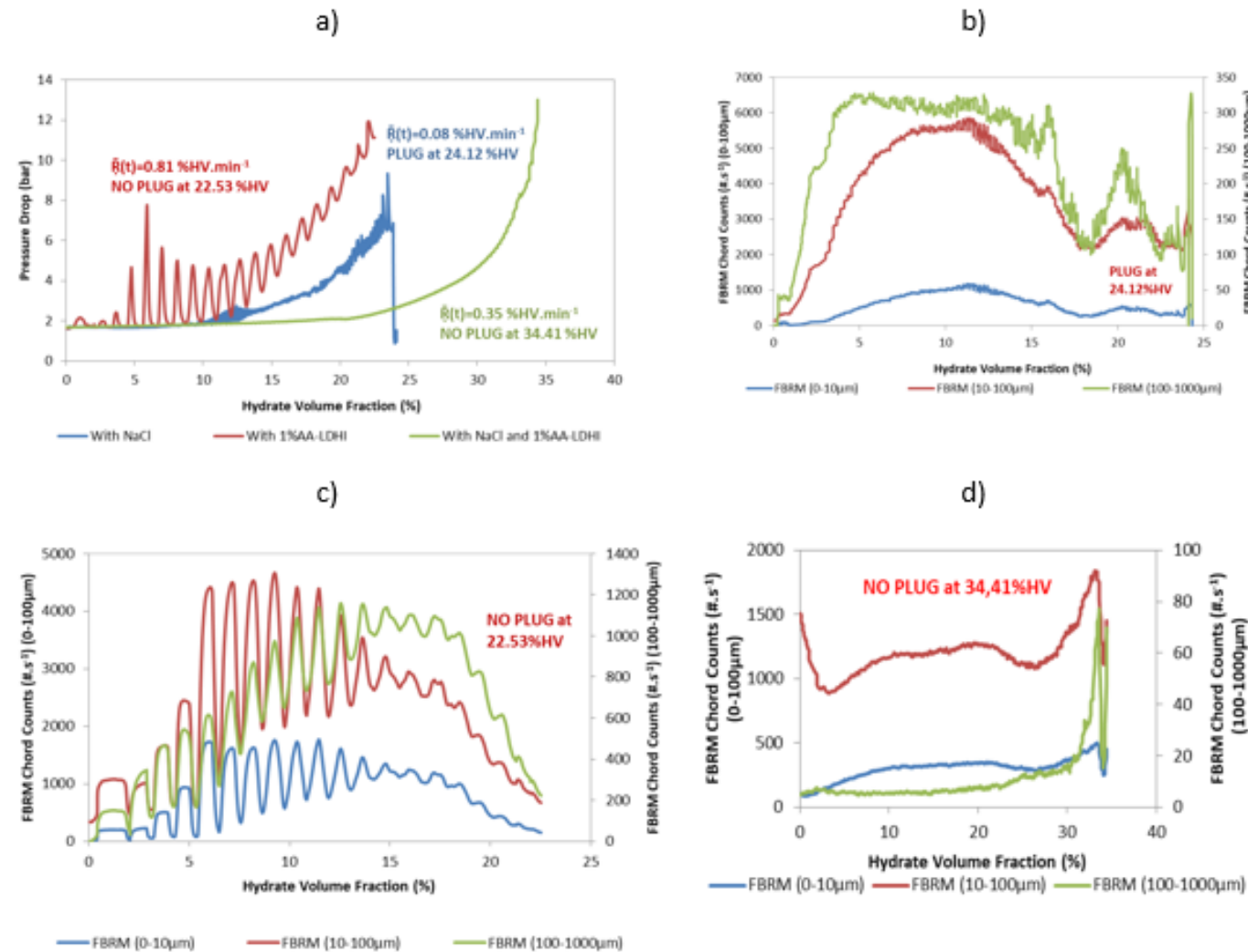


Fig. 11. Effect of a combination of salt and additive on hydrate slurry transport : (a) pressure drop; (b,c,d) FBRM chord counts versus hydrate volume fraction in the experiments of 100%WC-85%LV-75bar-400L.h-1 with NaCl - with 1%AA-LDHI - with NaCl and 1%AA-LDHI).

4. Results & Discussion

In preparation to
publish soon...



Effect of
combination of salt
and additive on
hydrate
transportability

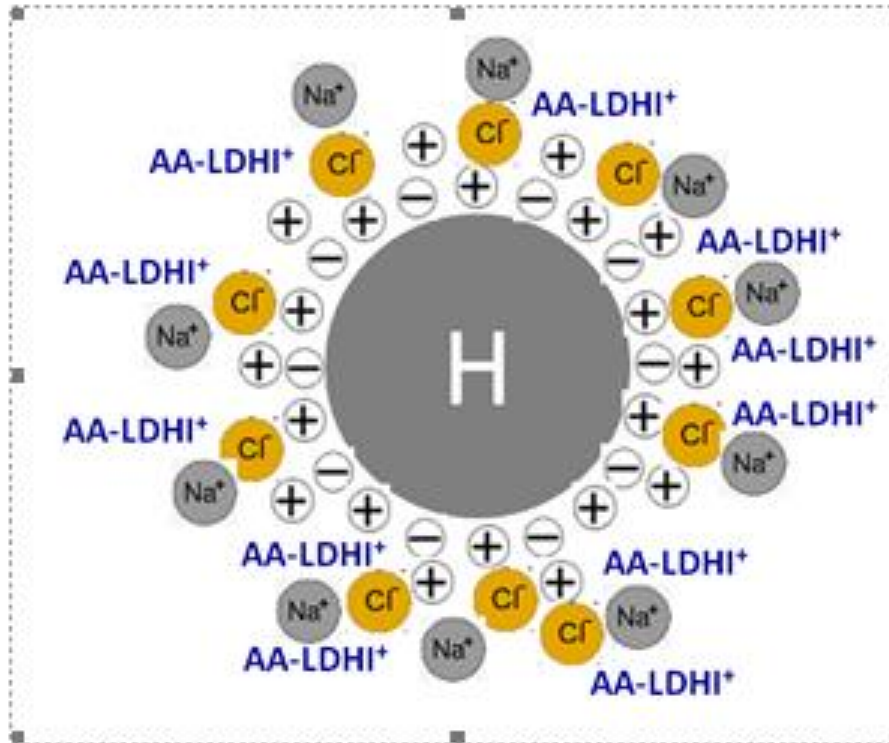


Fig. 12. Proposed mechanism of hydrate particle-AA-LDHI-salt interaction in preventing plug.

4. Results & Discussion

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Effect of water cut

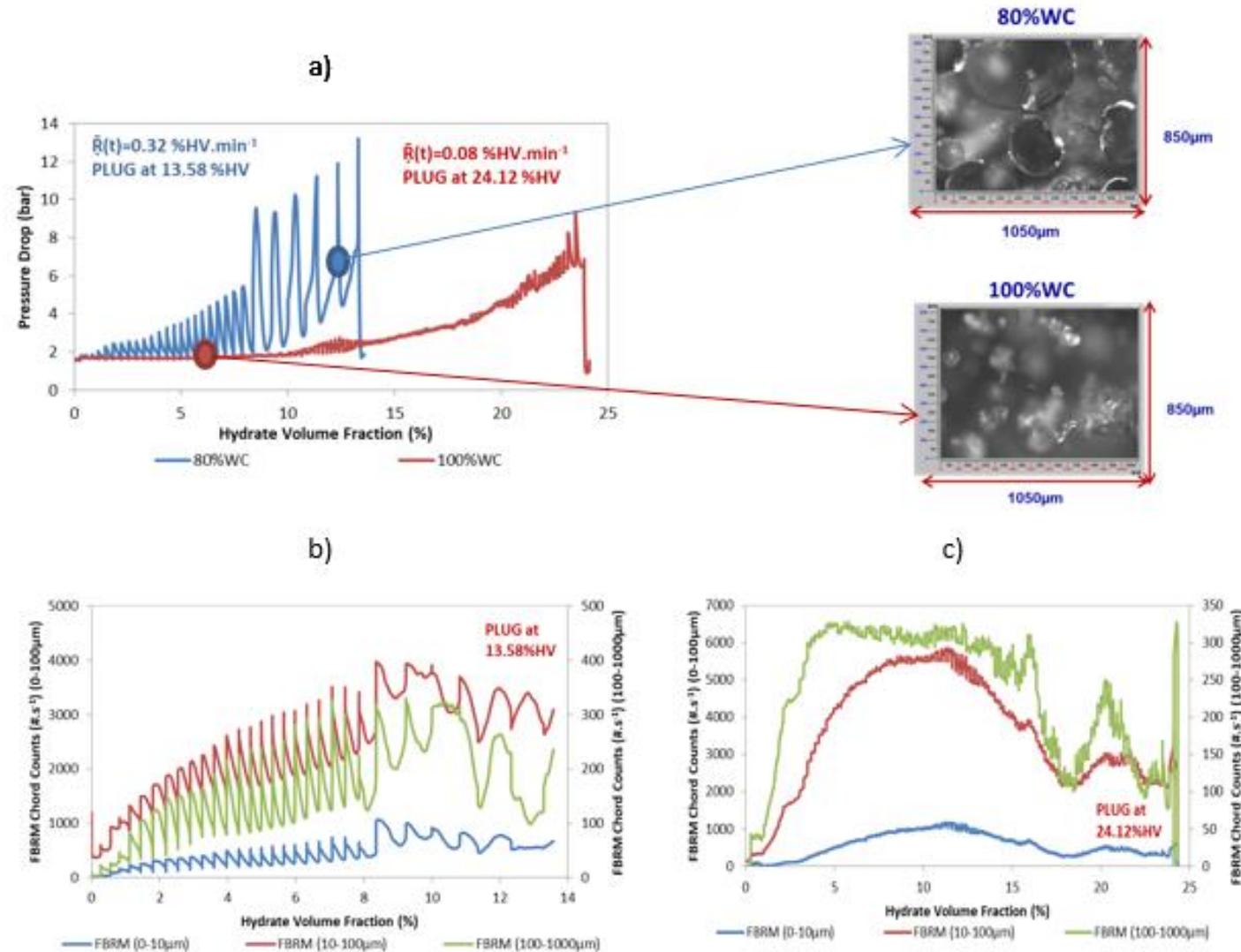


Fig. 13. Effect of water cut on hydrate slurry transport: (a) pressure drop; (b) FBRM chord counts at 80 and 100%WC versus hydrate volume fraction in the experiments of 80%WC and 100%WC-NaCl-85%LV-75bar-400L.h-1.

4. Results & Discussion

In preparation to
publish soon...



Effect of pressure

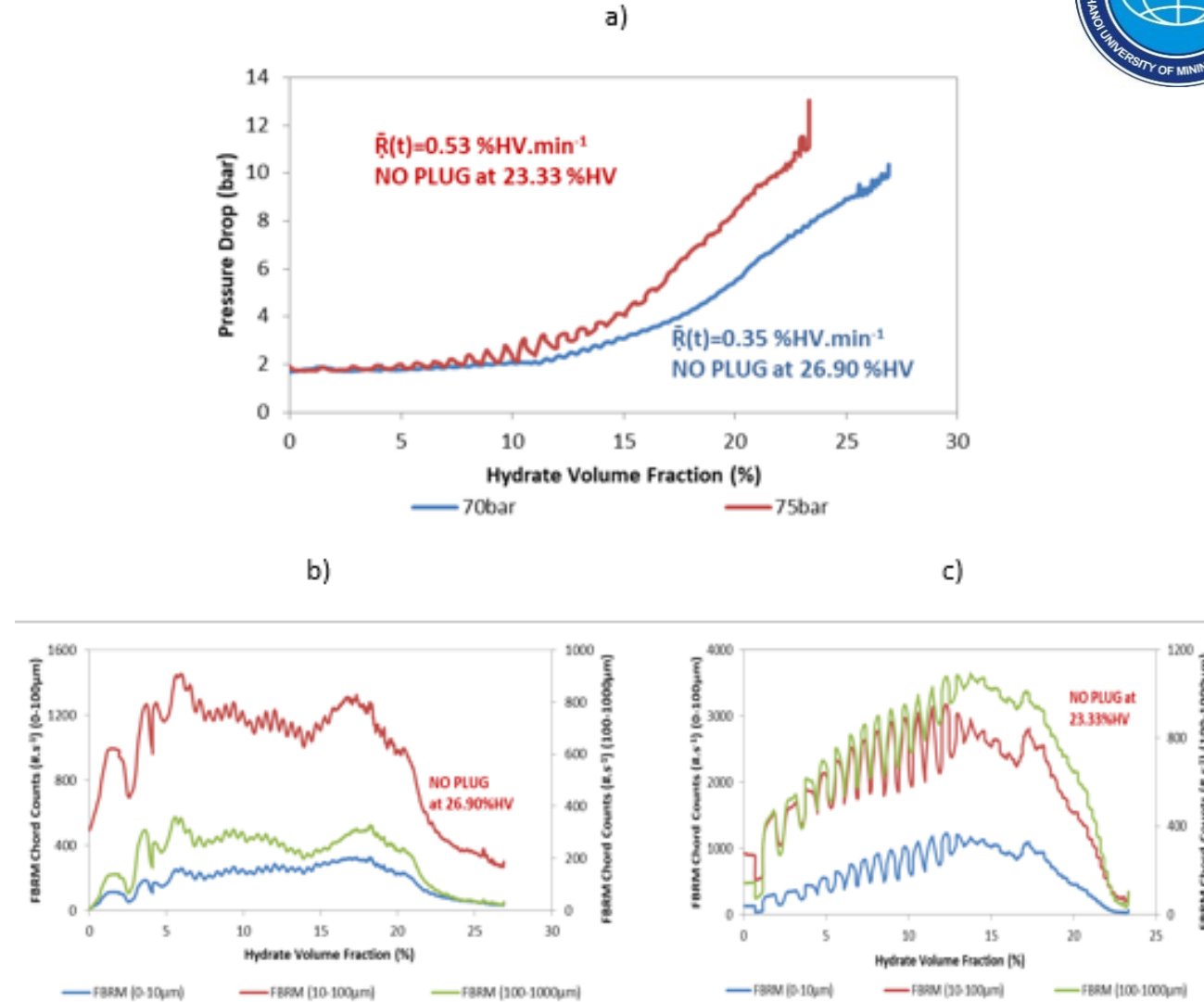


Fig. 14. Effect of pressure on hydrate slurry transport: (a) pressure; FBRM chord counts at 70 (b) and 75 bar (c) versus hydrate volume fraction in the experiments of 100%WC-2%AA-LDHI-85%LV-400L.h-1 at 70bar and 75bar.

4. Results & Discussion

Relative Pressure Drop Model

Trung-Kien PHAM, Ana CAMEIRAO, Aline MELCHUNA, Jean-Michel HERRI, Philippe GLENAT, "Relative pressure drop model for hydrate formation and transportability in flowlines in high water cut systems", Energies 2020, 13(3), 686



Relative viscosity (RV) model (Mills, 1985)

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

Relative pressure drop model

In laminar regime

$$\frac{\Delta P_{(t)}}{\Delta P_{(t_0)}} = \frac{\mu_{(t)}}{\mu_{(t_0)}} = \frac{1 - \Phi_{eff}}{\left[1 - \left(\frac{\Phi_{eff}}{\Phi_{max}}\right)\right]^2}$$

In turbulent regime

$$\frac{\Delta P_{(t)}}{\Delta P_{(t_0)}} = \left(\frac{\mu_{(t)}}{\mu_{(t_0)}}\right)^b = \left\{ \frac{1 - \Phi_{eff}}{\left[1 - \left(\frac{\Phi_{eff}}{\Phi_{max}}\right)\right]^2} \right\}^b$$

Developed model for
relative pressure drop (RPD)



$$\Delta P_r = \frac{\Delta P_{(t)}}{\Delta P_{(t_0)}} = \frac{1 - \Phi_{eff}}{\left[1 - \left(\frac{\Phi_{eff}}{\Phi_{max}}\right)^n\right]^2} \text{ and } \Phi_{max} = 0.74 \text{ (n=1.26)}$$

$$\Phi_{eff} = K_v \Phi$$



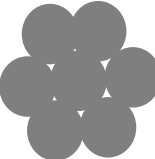
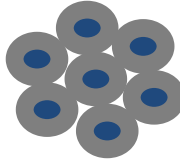
The higher value of K_v : the larger hydrate agglomerates (more heterogeneous flow), the larger liquid inside agglomerates, and the higher pressure drop.

4. Results & Discussion

Relative Pressure Drop Model

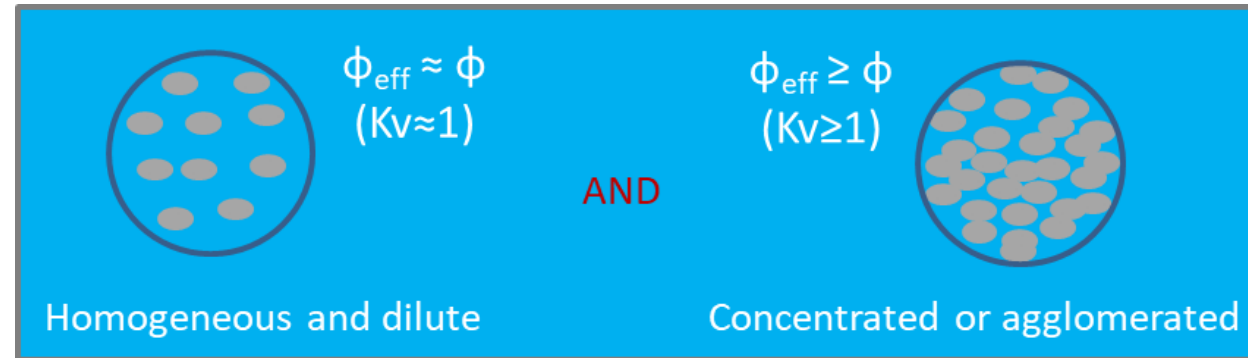
Trung-Kien PHAM, Ana CAMEIRAO, Aline MELCHUNA, Jean-Michel HERRI, Philippe GLENAT, "Relative pressure drop model for hydrate formation and transportability in flowlines in high water cut systems", Energies 2020, 13(3), 686



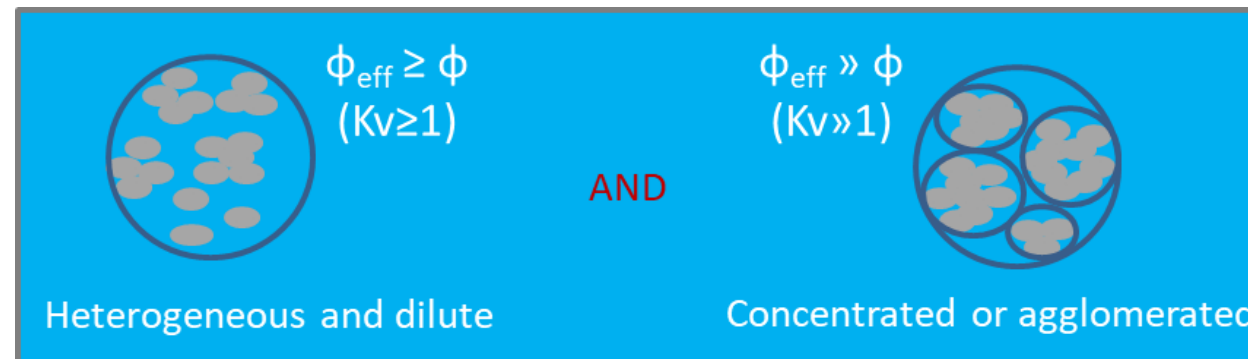
-  (1) Totally converted
 $K_v=1$
-  (2) Partially converted
 $K_v>1$
-  (3) Agglomerate with small (fully) particles
 $K_v\approx 1$
-  (4) Agglomerate with big (partially) particles
 $K_v\gg 1$

Fully (1) and partially (2) converted hydrate particle; and different hydrate agglomerates (3, 4)

Homogeneity (a)



Heterogeneity (b)



Hydrate agglomerate and liquid trapped inside:
(a) homogeneous and (b) heterogeneous hydrate suspension flow

4. Results & Discussion

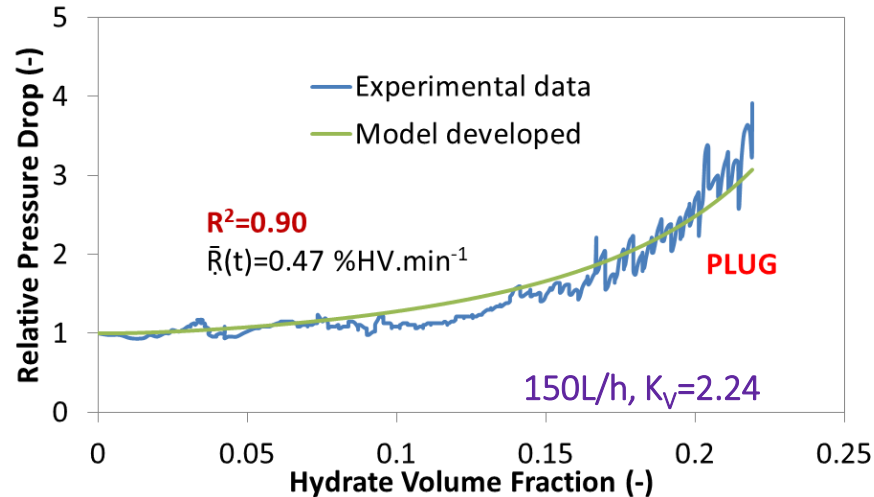
Relative Pressure Drop Model

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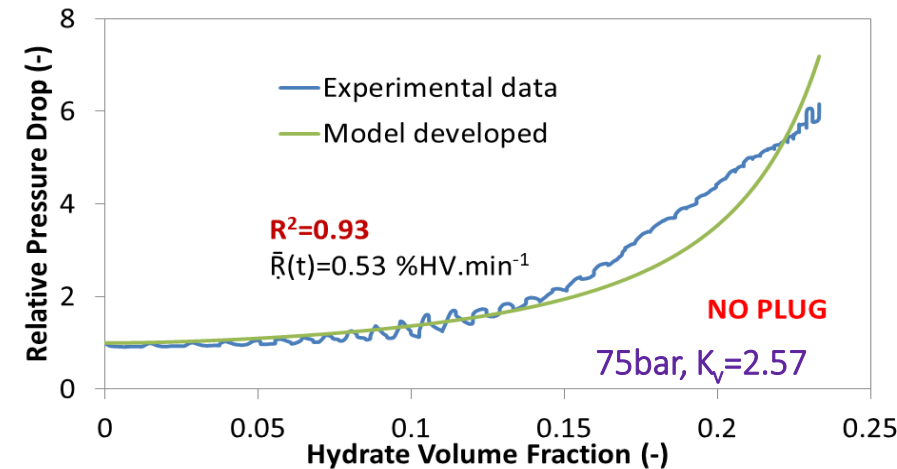
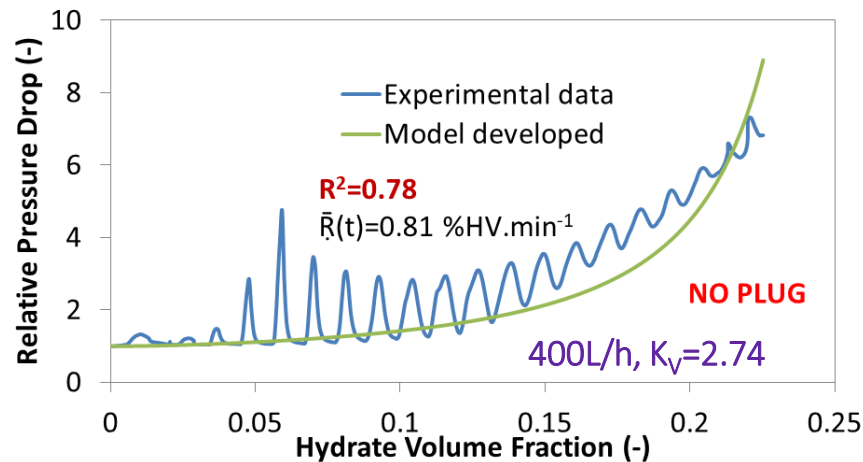
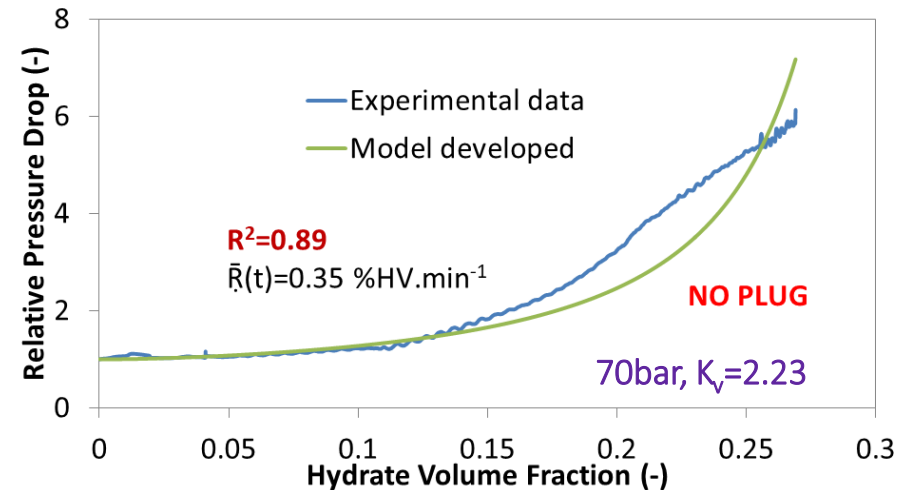
Effect of velocity

Higher velocities increased K_v



Effect of pressure

Higher pressure increased K_v



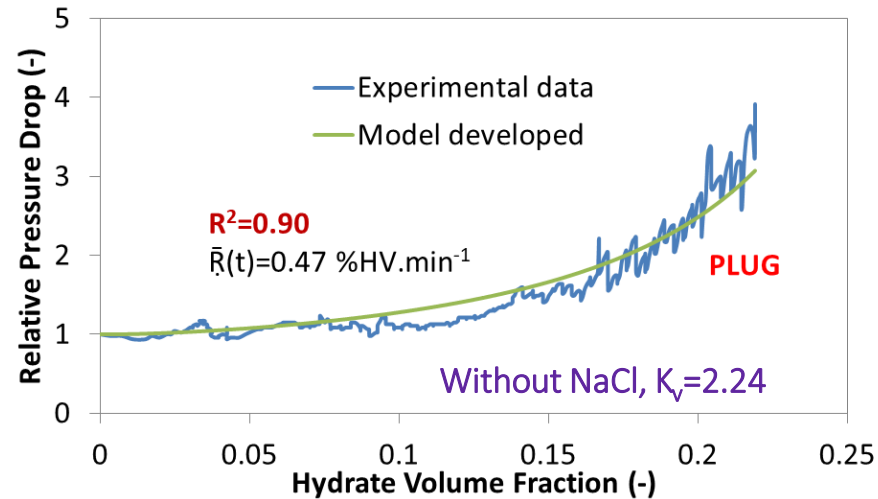
4. Results & Discussion

Relative Pressure Drop Model

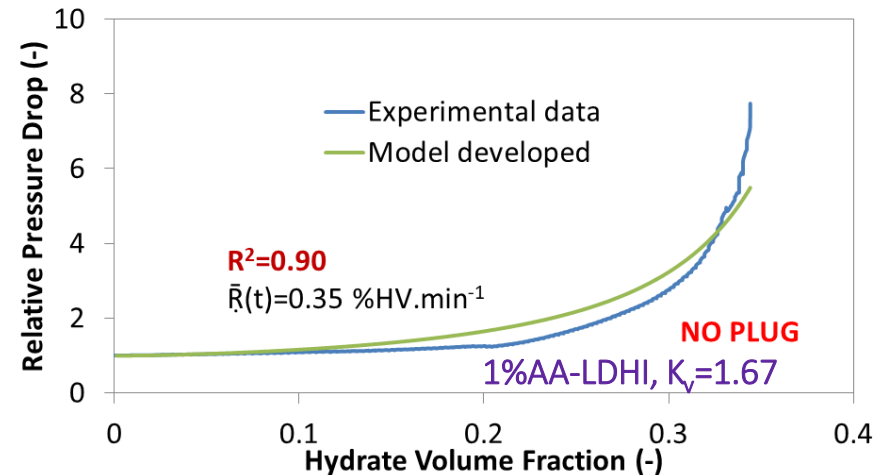
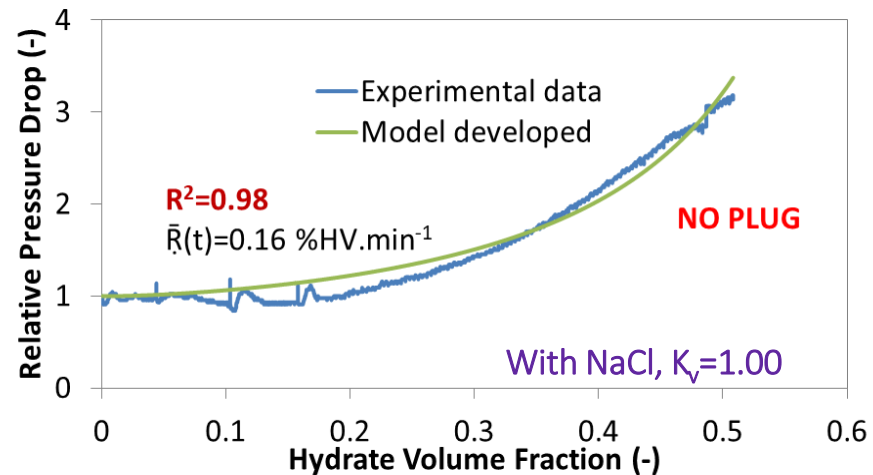
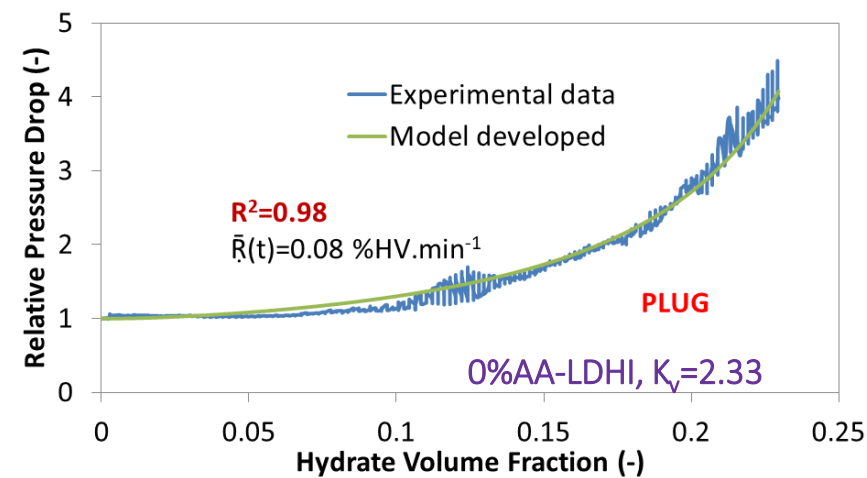
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Effect of salt



Effect of additive



4. Results & Discussion

Relative Pressure Drop Model

Model Evaluation

- The model results agree well with experimental data, especially with homogeneous flow
- This new model describes very well the hydrate agglomerate structures (K_v is between 1.00 and 2.74)
- The determination coefficient (R^2) stays in the range of 0.76 to 0.98

| WC | Flowrate | Liquid Volume | Pressure | AA-LDHI | NaCl | $\bar{R}(t)$ | Structural agglomerate factor | Coefficient of multiple determination | PLUG |
|-----|----------------------|---------------|----------|---------|--|--------------------------|-------------------------------|---------------------------------------|------|
| (%) | (L.h ⁻¹) | (%) | (bar) | (wt.%) | (g.L ⁻¹ (H ₂ O)) | (%HV.min ⁻¹) | (K_v) | (R^2) | - |
| 100 | 400 | 85 | 75 | 0.50 | 0 | 0.43 | 2.36 | 0.92 | YES |
| | 150 | 85 | 75 | 1 | 0 | 0.47 | 2.24 | 0.90 | YES |
| | 400 | 85 | 75 | 1 | 0 | 0.81 | 2.74 | 0.78 | NO |
| | 400 | 85 | 70 | 2 | 0 | 0.35 | 2.23 | 0.89 | NO |
| | 400 | 85 | 75 | 2 | 0 | 0.53 | 2.57 | 0.93 | NO |
| | 400 | 85 | 75 | 0 | 30 | 0.08 | 2.33 | 0.98 | YES |
| | 400 | 85 | 75 | 0.50 | 30 | 0.35 | 1.33 | 0.95 | NO |
| | 150 | 85 | 75 | 1 | 30 | 0.16 | 1.00 | 0.98 | NO |
| | 400 | 85 | 75 | 1 | 30 | 0.35 | 1.67 | 0.90 | NO |
| 80 | 400 | 85 | 75 | 1 | 0 | 0.72 | 2.22 | 0.83 | NO |
| | 150 | 85 | 75 | 1 | 30 | 0.10 | 1.12 | 0.76 | NO |
| | 400 | 85 | 75 | 1 | 30 | 0.18 | 1.73 | 0.95 | NO |

Trung-Kien PHAM, Ana CAMEIRAO, Aline MELCHUNA, Jean-Michel HERRI, Philippe GLENAT, "Relative pressure drop model for hydrate formation and transportability in flowlines in high water cut systems", Energies 2020, 13(3), 686





5. Conclusions & Perspectives

- Three main hydrate transport phenomena in high water cut systems are high pressure drop with plug, high and low pressure drop and flowing. Hydrate formation impacted on flowing and destabilized dispersion. Slow and quick heterogeneities are observed and agglomeration and deposition can be detected by FBRM, pressure drop, density, and PVM measurements.
- The increase in flowrate increased the average rate of crystallization and improved hydrate slurry transport. The use of different flowrates led to different agglomeration/deposition and plugging mechanisms.
- AA-LDHI can lower pressure drop, improve homogeneous flow and hydrate transport. However, AA-LDHI increases the rate of crystallization. The addition of adequate dosage of AA-LDHI lowered pressure drop, stabilized the hydrate slurry flow and helped hydrate slurry to flow more homogeneously and prevented plugging. The use of AA-LDHs probably changed the hydrate particle size, structure of agglomeration and deposition.

5. Conclusions & Perspectives

- Salt lowered the crystallization rate and impacted positively on the performance of AA-LDHI. Commonly, the addition of salt lowered significantly the average rate of crystallization and impacted positively on the performance of AA-LDHI such as lower pressure drop, less heterogeneous hydrate slurry flow, less hydrate deposition and avoided plugging. The role of salt to enhance the effectiveness of additive was interpreted by enhancement of additives adsorbed on the surface of hydrate particles and probably by phase inversion.
- The rise in water cut lowered the average rate of crystallization. In the presence of both AA-LDHI and salt, the increase in water cut enhanced the average rate of crystallization. Sphere shape was predominant along with the non-sphere shape of hydrate particles in the presence of the oil phase. Hydrate morphology at 100%WC was non-spherical.
- The increase in pressure augmented the average rate of crystallization. The increase in the average rate of crystallization led to quicker agglomeration and heterogeneity rates.



5. Conclusions & Perspectives

- A new model was proposed to predict the relative pressure drop in pipelines.
- An effective volume fraction factor (K_v) is used to describe the structure of hydrate agglomerates.
- A good agreement was obtained with experimental results.

6. Acknowledgements



1. SPIN Centre, Saint-Etienne School of Mines (EMSE)
2. Petroleum and Energy Faculty, Hanoi University of Mining and Geology (HUMG)
3. International Co-operation Office (EMSE and HUMG)
4. Oil Refining and Petrochemicals Department (HUMG)
5. Advanced Program in Chemical Engineering (HUMG)

