Methane hydrate crystallisation in pure water and influence of PVP additive
How we can extrapolate results from laboratory experiments to pilot scale experiments

*i.e.*

How geometry affects the crystallisation processes

---

**SYSTEM**

- water + methane
- Oil in water emulsion + methane
- Water in oil emulsion + methane

**GEOMETRY**

- Batch reactor
- Batch reactor
- « pilot » flow loop

**Scaling up**
EXPERIMENTAL SET-UP:

Semi-batch pressurized and stirred reactor

- Isothermal (1°C)
- Isobaric [30-100 bars] → gas consumption
- Liquid injection (inhibitor)
- Turbidity sensor
Turbidity sensor

Parallel light beam

Scattering events
Particle size determinations
Particle sizing using in situ spectral turbidimetry

**EXPERIMENTALS**

\[
\tau_{\lambda} = \frac{1}{L} \ln \frac{I_0}{I_L}
\]

**THEORY**

\[
\tau_{\lambda} = \frac{\pi}{4} \int_0^\infty Q_{\text{sca}}(\lambda, D, m) D^2 f(D) dD
\]

Crystal population density function \( f(D) \)
Batch tank
Pure water and methane
Pressure of 3 MPa
Temperature of 1°C

Stirring rate
- 250 rpm
- 300 rpm
- 350 rpm
- 400 rpm
- 450 rpm
- 500 rpm
- 600 rpm

![Graph a](image)

![Graph b](image)
THEORY
Processes considered

Two-layer model

Methane dissolution

\[ \frac{r}{V} = k_L a (C_{ext} - C) \]

\[ \delta = \frac{D}{k_L} \]

Surface layer

Bulk

\[ C_{ext} \]

\[ C \]

\[ H \]
EXPERIMENTAL RESULTS
Initially dissolved inhibitor

Influence on gas consumption rate

Long time experiments at 45 bar

Influence on gas consumption rate
3 steps

0% PVP K30
400 tr / min

1% PVP K30
400 tr / min

Gas consumption [mol]

Cbulk

nucleation

Cext

Ceq or C*

time

t-tL [s]
THEORY

Processes considered

\[
\frac{dC}{dt} = k_L a (C_{ext} - C) - \frac{4\pi}{\delta_m} GM^2
\]

Two-layer model

Surface layer

Bulk

\[ \delta = \frac{D}{k_L} \]

Methane dissolution

Primary nucleation

Primary nucleation

Secondary nucleation

Fragmentation

Growth

Agglomeration
THEROY
Fundamentals equations & solution method

1- Methane mass balance equation

\[
\frac{dC}{dt} = k_L a (C_{ext} - C) - \frac{4\pi}{\vartheta_m} GM_2
\]

2-population balance equation

\[
\frac{\partial f}{\partial t} + G \frac{\partial f}{\partial R} = (B_I + B_{II} + B_{III}) \delta(R) + A_g
\]

Moment method

\[
M_j = \int_0^\infty R^j f(R) dR
\]

\[
\frac{dM_0}{dt} = B_I + B_{II} + B_{III} + A_0
\]

\[
\frac{dM_j}{dt} = jGM_{j-1} + A_j \quad 1 \leq j \leq 5
\]
THEORY
Primary nucleation

Integration on interfacial layer

Local rate:

\[ B_I = k_1 \exp \left( -\frac{B}{\ln^2 \frac{C}{C_{eq}}} \right) \]

\[ B_{I,1} = \sum \frac{k_1}{V_L} \int_0^\delta \exp \left( -\frac{B}{\ln^2 S(z)} \right) \, dz \]

Bulk zone

\[ B_{I,2} = k_1 \exp \left( -\frac{B}{\ln^2 S_b} \right) \]

\[ S = \frac{C}{C_{eq}} \]

Surpersaturation
THEORY
Growth: introduction of a dead zone

- rate-determining step: diffusion
  \[ G_{\text{diff}} = k'_g (C_b - C^*) \]

- rate-determining step: growth
  \[ G_{\text{réac}} = k''_g (C_b - C^*)^p \quad p = 1 \text{ ou } 2 \]

\[ G = \min \left( G_{\text{diff}}, G_{\text{réac}} \right) \]
NUMERICAL SOLUTION
Parametric analysis

\[ P = 30 \text{ bar} \]

Primary nucleation + growth

- Linear increase of \( Np \)
- Average diameter = Constant
- Supersaturation near 1
Batch tank
Pure water and methane
Pressure of 3 MPa
Temperature of 1°C

Stirring rate
- 250 rpm
- 300 rpm
- 350 rpm
- 400 rpm
- 450 rpm
- 500 rpm
- 600 rpm

(a) mean diameter [µm]
(b) Particles density [#/cm³]

Elapsed time [min]
THEORY
Processes considered

Two-layer model

Surface layer

Bulk

\( \delta = \frac{D}{k_L} \)

\( C_{\text{ext}} \)

\( C \)

\( H \)

\( \frac{r}{V} = k_L a(C_{\text{ext}} - C) \)

Methane dissolution
« Experimental study and interpretation of the action of a kinetic inhibitor on methane hydrate crystallization »

• INVESTIGATED SYSTEM : PVP

Poly-N-Vinyl-2-Pyrrolidone

Tools :
Gas consumption recording + Particle sizing
EXPERIMENTAL RESULTS
Initially dissolved inhibitor

Different concentrations in PVP K30 (0 to 1% weight)

\( P = 45 \text{ bar} \)

Turbidity variation with time

**Induction time** \( t_L \)

\( \% \text{ PVP K30} \)

Formation : 45 bar ; 400 tr / min

Formation : 45 bar ; 550 cm\(^{-1}\)
EXPERIMENTAL RESULTS
Initially dissolved inhibitor

Influence of PVP on the steady consumption rate

\[ r_c \text{[mol / min]} \]

\[ P = 45 \text{ bar} \]

\[ \frac{r}{V} = k_L a (C_{ext} - C) \]

Stirring rate [rpm]

\%
PVP K30
ANALYTICAL MODEL
Phase 1: dead zone determination

Stationary consumption rate

\[
\frac{r_c}{V_L} = k_L a (C_{ext} - C^*)
\]

\[
C^* = C_{ext} - \frac{1}{k_L a V_L} \frac{r_c}{V_L}
\]

<table>
<thead>
<tr>
<th>Stationary consumption rate</th>
<th>Stationary consumption rate</th>
<th>Stationary consumption rate</th>
<th>Stationary consumption rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0E-05</td>
<td>5.5E-05</td>
<td>6.0E-05</td>
<td>6.5E-05</td>
</tr>
<tr>
<td>7.0E-05</td>
<td>7.5E-05</td>
<td>8.0E-05</td>
<td>8.5E-05</td>
</tr>
<tr>
<td>9.0E-05</td>
<td>9.5E-05</td>
<td>1.0E-04</td>
<td>1.0E-04</td>
</tr>
</tbody>
</table>

\( C^* \text{ [mol/mL]} \quad \omega = 300 \text{ tr/min} \)

\( C_{ext} \text{ (45 bar)} \)

\( C_{ext} \text{ (55 bar)} \)

\( C_{eq} \text{ (1°C; 29 bar)} \)

% PVP
EXPERIMENTAL RESULTS
Inhibitor injected during crystallization

$P = 45 \text{ bar} - \omega = 300 \text{ and } 400 \text{ rpm}$
EXPERIMENTAL RESULTS
Initially dissolved inhibitor

Influence on PSD

Increase in Np slower and slower

Lower decrease in $D_{\text{mean}}$
SIMPLIFIED ANALYTICAL MODEL

Main assumptions

• Rate-determining absorption: Concentration constant in bulk

• Crystal growth: existence of a dead zone for $C < C^*$

• Primary nucleation

\[
B_l = k_l G^n
\]

local

\[
C_{\text{bulk}} = C^*
\]

\[
B_l = b_0 + k_l (C_b - C^*)^q
\]

integrated

\[
b_0 = \frac{k_l k_g^n a\delta (C_{\text{ext}} - C^*)^{np}}{1 + np}
\]
Experimental results ➔ Two sources of crystals
**ANALYTICAL MODEL**

Phase 1: primary nucleation characterization

\[
b_0 = \frac{k_1 k_n^a \delta (C_{ext} - C^*)^{np}}{1 + np}
\]

Without additive

With PVP

\[\ln b_0 = \text{linear dependence against } \ln(\Delta C_M)\]

the same intercept

\[k_1 \text{ and } k_n \text{ are not affected by PVP, only } C^* \text{ varies}\]
Primary nucleation always active in the interfacial layer in presence of inhibitor (analytical model)

- Introduction of a wide dead zone $C^* > C_{eq}$
- Action on primary nucleation and growth rate
- Second source of crystals in later stages
- Long-range decrease of the inhibitor effect
Perspectives: extrapolate the model to real flow, that means:

1) To define what is a real flow

- gas
- oil
- Water

or

- gas
- Water in oil emulsion

2) To propose a crystallisation model

3) To couple with the rheology
3) To couple with the rheology

15.8% eau
0.08% IPE