Hydrodynamically constrained flux of in-situ generated methane hydrate dissolving into undersaturated seawater

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Hydrate stability in seawater

Hydrate dissolution at controlled hydrodynamic forcing: Rationale

![Graph showing hydrate stability](image)

- **P [MPa]**
- **T [°C]**

- **C_{CH_4} [mol/kg]**

- 20 MPa
- 10 MPa
- 5 MPa
Dissolution of hydrate - diffusion or reaction controlled?

\[ F = K' A (C_{sat} - C_{bckgr}) \]

\[ C_{bckgr} \] → bulk water (in motion)

\[ k_d = D/z \]

diffusive sublayer (stagnant)

\[ k_r \]

desorption layer

hydrate crystal

\[ \frac{1}{K'} = \frac{1}{k_d} + \frac{1}{k_r} \]

reaction controlled:

\[ K' = k_r \]

diffusion controlled:

\[ K' = k_d \]
Hydrate dissolution - Tools

Interfacial flux chamber „microcosm“

- Production of a radial flowfield at the hydrate/seawater interface in the flux chamber
- Almost constant, adjustable and calibrated friction velocity ($u^*$) over the entire surface

Peppe et al. (1999)
Friction velocities were set to 0.6, 1.0 and 1.2 cm/s for each temperature

<table>
<thead>
<tr>
<th>$T$ [°C]</th>
<th>$\rho$ [kg/m³]</th>
<th>$\mu$ [mPas]</th>
<th>$D/10^{-5}$ [cm²/s]</th>
<th>$C_{\text{sat}}$ [mmol/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1042</td>
<td>1.726</td>
<td>9.306</td>
<td>55.3 (209.9)</td>
</tr>
<tr>
<td>3.7</td>
<td>1041</td>
<td>1.638</td>
<td>9.859</td>
<td>61.4 (204.4)</td>
</tr>
<tr>
<td>9.0</td>
<td>1040</td>
<td>1.408</td>
<td>11.53</td>
<td>85.8 (189.4)</td>
</tr>
</tbody>
</table>

$c_{\text{sat}}$: Tishchenko et al. (2005)
Hydrate dissolution at controlled hydrodynamic forcing: Results

\[ C_t = C_{t0} + (C_{sat} - C_{to}) e^{-\left(\frac{A}{V}\right)kt} \quad t[h] \]
Hydrate dissolution - Results II

- Saturation concentration in good agreement with predictions according to Tishchenko et al. (2005)

- Change in T results in change of saturation concentration and thus, thermodynamic driving force of dissolution

- Friction velocity ($u^*$) has a strong impact on the dissolution rate

\[
\frac{1}{K'} = \frac{1}{k_d} \quad \frac{dn}{dt} = k_d A (C_{sat} - C_{bckgr})
\]

- Results strongly substantiate idea dissolution of methane hydrate in undersaturated seawater is a diffusion-controlled process
Hydrate dissolution - Results III

- Excellent agreement of measured transfer coefficients and those obtained from the dissolution of smooth alabaster plates demonstrates reliability of our data.

- Data yield a correlation for the flux of methane from decomposing hydrate outcrops for a broad range of P, T and $u^*$ conditions prevailing in the oceans on the seafloor.

$k_d = D/z$

\[ k_d = 0.078 \left( \frac{\mu}{\rho \cdot D} \right)^{-2/3} u^* \]

\[ z = 0.0173 u^{* -0.97} \]
Comparison with earlier data

current speed: 1.6 cm/s ->
\[ u^* = 0.07 \text{ cm/s} \]
\[ D = 10^{-5} \text{ cm}^2/\text{s} \]

\[ T = 0 \degree C \]
\[ P = 12 \text{ MPa} \]
\[ C_{\text{sat}} = 53.7 \text{ mmol/L} \]
\[ z = 2.3 \text{ mm} \]

50 m$^3$  
Egorov et al. (1999)

16.7 m$^3$  
this study
Comparison with earlier data

**Egorov et al. (1999)**
- Current speed: 1.6 cm/s
- $u^* = 0.07$ cm/s
- $D = 10^{-5}$ cm$^2$/s
- $T = 0^\circ$C
- $P = 12$ MPa
- $C_{sat} = 53.7$ mmol/L
- $z = 2.3$ mm

**this study**
- Current speed: ? cm/s
- $u^* = ?$
- $T = 3.5^\circ$C
- $P = 10.5$ MPa
- $C_{sat} = 69.8$ mmol/L
- $D = 10^{-5}$ cm$^2$/s
- $z = 1$ mm

**Rehder et al. (2004)**
- Current speed: ? cm/s
- $u^* = ?$
- $T = 3.5^\circ$C
- $P = 10.5$ MPa
- $C_{sat} = 69.8$ mmol/L
- $D = 10^{-5}$ cm$^2$/s
- $z = 2.3$ mm

**Hydrate dissolution at controlled hydrodynamic forcing: Application**

- $50$ m$^3$
- $16.7$ m$^3$
- $370$ µmol

- Egorov et al. (1999)
- this study
- Rehder et al. (2004)
Comparison with earlier data

**current speed: 1.6 cm/s ->**
- $u^* = 0.07 \text{ cm/s}$
- $D = 10^{-5} \text{ cm}^2/\text{s}$

**current speed: 1.75 cm/s ->**
- $u^* = 0.08 \text{ cm/s}$
- $T = 3.5 \degree \text{C}$
- $P = 10.5 \text{ MPa}$
- $C_{\text{sat}} = 69.8 \text{ mmol/L}$
- $D = 10^{-5} \text{ cm}^2/\text{s}$

<table>
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<tr>
<td>50 m³</td>
<td>16.7 m³</td>
<td>370 µmol</td>
</tr>
<tr>
<td>$T, P, C_{\text{sat}} = ?$</td>
<td>$T = 0 \degree \text{C}$</td>
<td>$z = 0.179 \text{ mm}$</td>
</tr>
<tr>
<td>$z = 1 \text{ mm}$</td>
<td>$z = 2.3 \text{ mm}$</td>
<td>$z = 2.3 \text{ mm}$</td>
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Hester et al., pers. comm.
## Comparison with earlier data

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<tr>
<td>Current speed</td>
<td>1.6 cm/s</td>
<td></td>
<td>1.75 cm/s</td>
<td></td>
</tr>
<tr>
<td>$u^*$</td>
<td>0.07 cm/s</td>
<td></td>
<td>0.08 cm/s</td>
<td></td>
</tr>
<tr>
<td>$D$</td>
<td>$10^{-5}$ cm$^2$/s</td>
<td></td>
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<td></td>
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<td>53.7 mmol/L</td>
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<td>$z$</td>
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**50 m$^3$**
- Egorov et al. (1999)
- **16.7 m$^3$**
- this study

**370 µmol**
- Rehder et al. (2004)
- **33.4 µmol**
- this study

*Hester et al., pers. comm.*

Hydrate dissolution at controlled hydrodynamic forcing: Application
Comparison with earlier data

Ocean experiment:
- Cylindrical hydrate specimens in cross flow

Lab:
- Plain surfaces in parallel flow
Conclusion/outlook

- Dissolution experiments demonstrate that hydrate dissolution in undersaturated seawater at $P$-/$T$-conditions within the HSF is diffusion and not reaction controlled.

- Based on the experimental data, a $k_d/u^*$ correlation was obtained, which excellently agrees with and is thus validated by an earlier correlation obtained from dissolution experiments with alabaster plates.

- The validated correlation permits an accurate prediction of the dissolution rates of smooth and clean methane hydrates exposed to a flow of undersaturated seawater for a broad range of oceanic conditions.

- Comparison with earlier data and postulations shows significant discrepancies. In one case this was due to a different sublayer thickness, which for lack of available data has been poorly constrained before.

- Future studies should address the role of inhibitors such as sediments or bacterial mats covering most natural gas hydrates.
Relevant Experiments I

Effect of flow:

- Flux of Ca and SO$_4$ determined from mass loss of the alabaster
- A diffusive boundary layer model was assumed to explain mass loss.
- $k = 0.078 \text{ Sc}^{-2/3} u^*$

*GRL 1987, 14, 1131-1134*
• Results of the field experiment fit well into a diffusive boundary layer model

• Dissolution of hydrates appears to be diffusion limited, not by kinetics of a chemical reaction

Rehder et al. (2004)

\[ F = \frac{D}{z} \left( C_{\text{sat}} - C_{t0} \right) \]

\[ z(\text{CO}_2) = z(\text{CH}_4), \quad D(\text{CO}_2) = D(\text{CH}_4), \quad C_{t0} = 0 \]

\[ \frac{F(\text{CO}_2)}{F(\text{CH}_4)} = \frac{C_{\text{sat}}(\text{CO}_2)}{C_{\text{sat}}(\text{CH}_4)} \]
Idea/Motivation

CH₄ hydrate dissolution at controlled hydrodynamic forcing

Estimated inventory of hydrate-fixed CH₄ in natural gas hydrates

after Sloan and Koh, 2007

J. Greinert, IFM-GEOMAR
Comparison with earlier data

Current speed: 1.6 cm/s →
$u^* = 0.07$ cm/s

$D = 10^{-5}$ cm$^2$/s

$T, P, C_{sat} = ?$

$z = 2.3$ mm

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Current speed: 1.75 cm/s →
$u^* = 0.08$ cm/s

$T = 3.5^\circ$ C

$P = 10.5$ MPa

$C_{sat} = 69.8$ mmol/L

$D = 10^{-5}$ cm$^2$/s

$z_\text{ocean} / z_\text{lab}$ = 11.6

$\text{Flux}_\text{lab} / \text{Flux}_\text{ocean}$ = 11.1

$z = 2.08$ mm

$\text{CH}_4$ hydrated dissolution at controlled hydrodynamic forcing

$21.7$ m$^3$

Egorov et al. (1999)

$17.4$ m$^3$

this study

$30.6$ mmol

Rehder et al. (2004)

$33.4$ μmol

this study