Rapid Simulation of Solid Deposition in Cryogenic Heat Exchangers

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Outline & Co-Authors

1. RasGas LNG Train 4 Case Study
   a. ThermoFAST – calculating solid solubility
   b. CryoFAST – when, where, symptoms & solutions
3. Application of CryoFAST to RasGas Case Study
   a. Insight
   b. Possible remediation

Corey Baker
Jordan Oakley
Darren Rowland
Zach Aman
Option for two configurations:

- Heavy LNG: Scrub column overheads go straight to MCHE
- Lean LNG: Scrub column overheads go to NGL recovery first
Operated without problems through 2014 prior to planned shut down. Successful re-start in August 2014

Over 2 months, observed slight drift up in $\Delta p$ across MCHE but also slight increase in volumetric flow rate.

Does this indicate a problem?
Problem confirmed (adapted from Ismail & Al Thani, LNG-18, Perth 2016)

After 8-10 weeks, operational data were finally unambiguous. Normalised $\Delta p$ changes to account for flow rate variations compared with data from Train 5.
Sloughing at cold end of MCHE (adapted from Ismail & Al Thani, LNG-18, Perth 2016)

Suggests it is due to restriction in coldest section of MCHE. However, warming the cold bundle was not generally effective at mitigating or removing problem.
Water content of MCHE feed gas
(adapted from Ismail & Al Thani, LNG-18, Perth 2016)

Include data from steady operation earlier in the year.
No evidence of any violation of 1 ppm spec
Acid Gas Rejection Unit (AGRU) of Train 4 known to slightly underperform with repeated occurrences of gas having CO$_2$ content > 50 ppm. Clear culprit?
One clear event of off-spec gas (C$_{5+}$ > 0.2 mol%) correlated with start of increasing $\Delta p$. (2$^{\text{nd}}$ event irrelevant as train in Lean LNG mode)

But doesn’t explain continuous increases in $\Delta p$, which requires continued carryover.
Shut-down, thaw & analyse
(adapted from Ismail & Al Thani, LNG-18, Perth 2016)

And the winner is...

100 Litres of WATER!!

How is this possible??
Check cumulative water into MCHE 
(adapted from Ismail & Al Thani, LNG-18, Perth 2016)

Over period of 4 months, 170 kg water entered MCHE at < 1 ppm mole fraction. 
But what caused 100 kg to accumulate in MCHE given such low feed concentration?
Operators didn’t worry about the very brief loss of reflux on start-up in Train 4.
Likely explanation? Need GPA Research (adapted from Ismail & Al Thani, LNG-18, Perth 2016)

C$_{5+}$ carryover that occurred briefly during start-up froze out in cold bundle region of MCHE. Small impact on $\Delta p$.

Deposit acted as an adsorption site where low concentrations of H$_2$O (& CO$_2$) could accumulate and form significant blockage.
Need for a risk assessment tool

Brief 50 s upset during start-up led to plant shut down 4 months later. By time operating data showed problem existed, it was too late. Could operators have done something earlier to avoid shut down? Perhaps if they had access to appropriate tool for assessing risk?

Such a tool should predict:
- whether solids would freeze out
- where & when solids would deposit in MCHE
- operational symptoms
- possible early remediation strategies.
### Generating Solubility Curves for LNG

#### RasGas Feed Compositions to MCHE

<table>
<thead>
<tr>
<th></th>
<th>Normal Operating Condition</th>
<th>Upset Condition (C$_5^+$ Carry Over)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.000040</td>
<td>0.000040</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.909329</td>
<td>0.907510</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.057492</td>
<td>0.057377</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.021953</td>
<td>0.021910</td>
</tr>
<tr>
<td>iC$<em>4$H$</em>{10}$</td>
<td>0.004239</td>
<td>0.004230</td>
</tr>
<tr>
<td>nC$<em>4$H$</em>{10}$</td>
<td>0.006847</td>
<td>0.006833</td>
</tr>
<tr>
<td>iC$<em>5$H$</em>{12}$</td>
<td>0.000028</td>
<td>0.000596</td>
</tr>
<tr>
<td>nC$<em>5$H$</em>{12}$</td>
<td>0.000026</td>
<td>0.000544</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{14}$</td>
<td>0.000021</td>
<td>0.000441</td>
</tr>
<tr>
<td>C$<em>7$H$</em>{16}$</td>
<td>0.000021</td>
<td>0.000441</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.000004</td>
<td>0.000078</td>
</tr>
</tbody>
</table>

![Graph showing solubility curves for benzene](image)

- **Solid** (High Risk of Deposition)
- **Dissolved** (Safe Zone)
ThermoFAST

ThermoFAST [Beta 1.0.1]

- FLUID
- MODELS
- COMPOSITION
- FLASH
- SOLIDS
- HYDRATES

Saved Fluid: Custom Mixture

Available:
- Water
- Nitrogen
- Carbon Dioxide
- Hydrogen Sulphide
- Methane
- Ethane
- Propane
- isoButane
- n-Butane
- Cyclobutane
- isoPentane
- n-Pentane

Selected:

Add New  Move Selected  Clear All

View Properties
ThermoFAST: Select components
ThermoFAST: Define composition
ThermoFAST: Generate Solubility Curve
Predicting solids solubility: ThermoFAST

Fugacity of pure solid calculated from properties of pure substance only

\[
\ln(f_i^S) = \ln(\varphi_{pure,i}^L P) - \frac{\Delta H_{f,i}}{RT_{m,i}} \left[ \frac{T_{m,i}}{T} - 1 \right] + \frac{\Delta c_{p,i}^{L\rightarrow S}}{R} \left[ \frac{T_{m,i}}{T} - 1 + \ln \left( \frac{T}{T_{m,i}} \right) \right] - \frac{\Delta v_i^{L\rightarrow S}(P - P_m)}{RT}
\]

Use cubic EOS to describe fluid mixture in eqbm with solid EOS handles pressure & broad range of concentrations

\[
x_i = \frac{f_i^S}{\varphi_i^L P}
\]

Cubic EOS used to calculate \( \varphi_i^L \) in liquid mixture. \( \varphi_i^L \) depends on binary interaction parameter

BIPs optimised by tuning to literature SLE data

Iterative flash calculation until phase fractions & compositions become fixed.
ThermoFAST: Literature comparison

Also compare with Kohn Luk’s Solid Solubility Program (KLSSP):

\[
C_1 + \text{Benzene}
\]

\[
\begin{array}{ccccccc}
T / °F & & & & & & \\
-298 & -258 & -218 & -178 & -138 & -98 & \\
\end{array}
\]

\[
\begin{array}{ccccccc}
T / K & & & & & & \\
90 & 110 & 130 & 150 & 170 & 190 & 210 \\
\end{array}
\]

- Kuebler & McKinley (1974)  
- ThermoFAST  
- KLSSP
Comparisons with literature SLE data

Captures pressure dependence too (does not assume at bubble point)

$C_1 + \text{n-Hexane}$

$T / ^\circ\text{F}$

$T / \text{K}$

Hexane / mol fraction

- Shim & Kohn (1962)
- Dickinson et al. (1973)
- Kuebler & McKinley (1974)
- Luks et al. (1981)

ThermoFAST

KLSSP
Comparisons with literature SLE data

Extended to components not covered by KLSSP

**C₁ + Toluene**

T / °F
-298 -278 -258 -238 -218 -198 -178 -158

T / K
90 110 130 150 170

Toluene / mol fraction

- Kuebler & McKinley (1974)  
- ThermoFAST
Simulating where & when deposit occurs

Expansion Valve (Further Cooling)

Mixed Refrigerant Temperature Profile
~(110K to 200)K

Liquefied Gas (LNG)
~122K (-151°C)

Vapour + Liquid Region

Liquid Only

Increased insulation

INLET: (99 to 100) mol% vapour

Distillation Column Overhead Product
>85mol% CH₄ (210 to 240) K

Reduced Pipe Diameter

↑ velocity

↑ ΔP

Process Upset: Heavy carry-over!

MODELS

- Equation of State + Solid Equation
- Material Balance
- Momentum Balance (Steady-State)
- Energy Balance (Heat Transfer)

OUTPUTS

- Vapour, Liquid + Solid Fractions
- Mass Flow Rates + Mass Deposition
- Pressure Drop + Phase Velocities
- Exit Temperatures, Limitations due to Deposition
**Use CryoFAST to simulate the impact of C_{5+} carryover for 50 s**

Estimates based on detail provided by Ismail & Al Thani, and/or literature publications for similar systems

**Key Questions:**

a) Where & how much benzene will deposit?

b) Symptoms?

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Mass Flow Rate / tpd</td>
<td>12,603</td>
</tr>
<tr>
<td>Feed Temperature / K</td>
<td>250</td>
</tr>
<tr>
<td>Feed Pressure / MPa</td>
<td>5.0</td>
</tr>
<tr>
<td>Wall Roughness / mm</td>
<td>0.001</td>
</tr>
<tr>
<td>Tube Length / m</td>
<td>67</td>
</tr>
<tr>
<td>Number of Tubes</td>
<td>1,300</td>
</tr>
<tr>
<td>Internal Diameter / mm</td>
<td>14.0</td>
</tr>
<tr>
<td>Average Coil Diameter / m</td>
<td>2</td>
</tr>
<tr>
<td>Coil Pitch / m</td>
<td>1.11</td>
</tr>
<tr>
<td>Tube Inclination / degrees</td>
<td>10</td>
</tr>
<tr>
<td>Overall Local Heat Transfer Coefficient / W·m^{-2}·K^{-1}</td>
<td>900 to 2,500[Profile Range]</td>
</tr>
<tr>
<td>Refrigerant Temperature / K</td>
<td>112 to 234[Profile Range]</td>
</tr>
</tbody>
</table>
RasGas case study results

CryoFAST predicts 50 s upset in reflux would have produced:

1) Benzene deposition within 14 seconds, 92% of the way through the MCHE (i.e. in upper cold bundle).

2) Change in total pressure drop of +0.05% ⇒ not measurable

3) Max change in mass flow rate of -0.06% ⇒ not measurable

4) Effluent temperature change +8 K in 122 K
   ≈ +3% in refrigeration duty if effluent T controlled.

5) About 18 g of Benzene deposited per tube, reducing effective pipe diameter from 14 to 13.7 mm over last 4 m.

Small benzene deposit should have been removed when feed composition returned to normal!
How does hydrate or ice even form?

What do we estimate under normal operating conditions?

Pressure = 3.2 MPa

The pressure close to the benzene deposit

<table>
<thead>
<tr>
<th>Formation Temperature</th>
<th>Normal Operating Condition</th>
<th>Hydrate (Type II) Infochem CPA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrate (Type II)</strong></td>
<td>206.6 K [-87.83°F]</td>
<td></td>
</tr>
<tr>
<td>Infochem CPA</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ice Formation</strong></td>
<td>203.7 K [-93.01°F]</td>
<td></td>
</tr>
<tr>
<td>ThermoFAST</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Normal Operating Condition</th>
<th>Hydrate (Type II) Infochem CPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.000012</td>
<td>85.075100</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.004000</td>
<td>0.000309</td>
</tr>
<tr>
<td>CH₄</td>
<td>90.932900</td>
<td>9.999702</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>5.749200</td>
<td>1.586518</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>2.195300</td>
<td>3.046060</td>
</tr>
<tr>
<td>iC₄H₁₀</td>
<td>0.423900</td>
<td>0.271583</td>
</tr>
<tr>
<td>nC₄H₁₀</td>
<td>0.684700</td>
<td>0.020684</td>
</tr>
<tr>
<td>iC₅H₁₂</td>
<td>0.002800</td>
<td>0.000000</td>
</tr>
<tr>
<td>nC₅H₁₂</td>
<td>0.002600</td>
<td>0.000000</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>0.002100</td>
<td>0.000000</td>
</tr>
<tr>
<td>C₇H₁₆</td>
<td>0.002100</td>
<td>0.000000</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.000400</td>
<td>0.000004</td>
</tr>
</tbody>
</table>

0.12 ppm
Simulations with CryoFAST indicate dissolution of 18 g C\textsubscript{6}H\textsubscript{6} deposit should have taken \(\approx\) 37 hours with normal feed gas deposit.

⇒ In 37 hours, enough water adsorbed on benzene to make water crystallisation self-sustaining.

At average crystallisation rate \(\approx\) 1.1 g of H\textsubscript{2}O per tube.

Maximum window of opportunity to remediate benzene deposition is 37 hours.

Use CryoFAST to assess three possible remedial actions operators could have taken immediately:

(i) Raise temperature of cold bundle by 2 K
(ii) Reduce feed’s C\textsubscript{5+} content by factor of 2.
(iii) Combine (i) & (ii)

Drive scrub column condenser harder? Done in Nov 2014
Prospective remedial action efficacy

Rapid remedial actions operators could have taken if tool available:

(i) Raise temperature of cold bundle by 2 K.
Solubility of C\textsubscript{6}H\textsubscript{6} in LNG increases from 4 to 5.3 ppm. Removal time reduced from 37 to 7 hours.

(ii) Halve feed’s C\textsubscript{5+} content
Concentration of C\textsubscript{6}H\textsubscript{6} in LNG decreases from 3.7 to 1.9 ppm. Removal time reduced to 5 hours.

(iii) Combine (i) & (ii): Removal time reduced from 37 to 3 hours.

Analysis suggests an order of magnitude reduction in risk if strategy (iii) can be identified and implemented rapidly.
Conclusions

New simulation tools developed for assessing risk of solid formation & deposition in cryogenic heat exchangers

- *ThermoFAST* – optimised to accurately represent SLE, SVE & SLVE over wide range of conditions
- *CryoFAST* – solves energy & material balances to determine when & where solids form in spiral wound HXs

Applying tools to RasGas Train 4 case study of Ismail & Al Thani suggests:

- Cooling duty may be better than $\Delta p$ for operational symptoms
- 37 hour maximum window for dealing with initial blockage
- Ideal remediation strategy should remove blockage in 3 hours
THANK YOU

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http://lngfutures.edu.au/

Australian Government
Australian Research Council

http://www.fsr.ecm.uwa.edu.au
http://lngfutures.edu.au/
C3MR Section of Train 4
(from Ismail & Al Thani, LNG-18, Perth 2016)
ThermoFAST flash algorithms

Specify T, P, z

Calculate for each component i $f_{s,i}$ (Solid Model)

Set $L = 1, \sum s_i = S_F = 0$
Set $x_i = z_i$ for each i

Calculate $\varphi_i^L$ (EOS)

Calculate $x_i = \frac{f_i}{\varphi_i^L}$

Calculate $s_i = z_i - x_i L$
$L_{next} = 1 - \sum s_i$

$L = L_{next}$

Output $S_f, L_f, x_i$

Specify T, P, z

Solve VLE flash
Output $\beta, x, y$

Set $S_F = \sum s_i = 0$

$\sum L = 1 - \beta - S_F = 0$?

NO

Solve SLE flash on $x_i$ only
Output $s_i, L_{SLE}, x_i$

Calculate $s_i = s_i + (1 - \beta) s_{i, SLE}$

Combine the non-solid phase
$v_{SLE} = L_{SLE} ((1 - \beta)x_i) + \beta y_i$
$\rightarrow$ Normalise $v_{SLE}$

Output $s_i, L_{SLE}, L_{SLE}, y_i$

SLE only

SLVE

Solve pseudo SLE flash on $y_i$ only

Calculate $s_i = s_i + \beta s_{i, SLE}$

Combine the non-solid phase
$v_{SLE} = (1 - \beta)x_i + L_{SLE} (\beta y_i)$
$\rightarrow$ Normalise $v_{SLE}$

Solve VLE flash on non-solid phase, $z_{VLE} \rightarrow$ Output $\beta, x, y$

NO: Set $S_F = \sum s_i$

$S_F = \sum s_i$?

YES

Phase Amounts
$V = \beta (1 - \sum s_i)$
$L = 1 - V - \sum s_i$

Output $V, L, y_i, x_i, s_i$
Comparisons with literature SLE data

Cubic EOS can cover a wide concentration range

\[ C_1 + \text{n-Octane} \]

\[ T / \degree F \]

Octane / mol fraction

\[ T / K \]

- Kohn & Bradish (1964)
- Kohn et al. (1977)
- ThermoFAST
- KLSSP
Comparisons with literature SLE data

Not just tuned to methane binaries

\( C_2 + \text{Benzene} \)

\[ T / ^\circ \text{F} \]

\[ T / \text{K} \]

\[ \text{Benzene / mol fraction} \]

\( 10^{-2} \quad 10^{-1} \quad 1 \)

Liu et al. (1977)  ThermoFAST  KLSSP
Comparisons with literature SLE data

Activity coefficient models have limited concentration & pressure ranges

C$_1$ + n-Heptane

$T / ^\circ\text{F}$

Heptane / mol fraction

$T / \text{K}$


ThermoFAST  ●  ●  KLSSP
Material & energy balances

Guess node temp, \( T_{\text{out}} \), do flash & evaluate residence time for node

\[
u_n = \frac{\dot{m}}{\rho_n V}, \quad \Delta t = \frac{L}{u_n}
\]

Solve material balance

\[
\chi S_F \rho_n V = m_{\text{dep}} = (\dot{m}_{\text{in}} - \dot{m}_{\text{out}}) \Delta t
\]

\[
m_{\text{dep},i} = (\dot{m}_{\text{in}} w_{i,\text{in}} - \dot{m}_{\text{out}} w_{i,\text{out}}) \Delta t
\]

Solve energy balance for enthalpy & use EOS to get new estimate of \( T_{\text{out}} \) from \( h_{\text{out}} \).

\[
\frac{1}{\Delta t} \sum m_{\text{dep},i} \Delta h_{\text{fus},i} = \dot{m}_{\text{in}} \left( h_{\text{in}} + \frac{u_{\text{in}}^2}{2} + gz_{H,\text{in}} \right) - \dot{m}_{\text{out}} \left( h_{\text{out}} + \frac{u_{\text{out}}^2}{2} + gz_{H,\text{out}} \right) + \dot{Q}
\]

Iterate until consistent value of \( T_{\text{out}} \) found.
Centrifugal and twisting effects

Typical pressure drops found in coil wound heat exchangers due largely to twisting and centrifugal effects

\[
\kappa = \frac{R_c/R}{(R_c/R)^2 + (\Lambda_c/2\pi R)^2}
\]

\[
\tau = \frac{\Lambda_c/2\pi R}{(R_c/R)^2 + (\Lambda_c/2\pi R)^2}
\]

\[
D_e = Re \sqrt{\kappa}
\]

\[
Ge = Re \tau
\]

\[
f_R = 1 + 0.0167 \frac{D_e^{1.5}}{Ge}
\]

![Pressure Drop Diagram]