THE ROLE OF TRANSPORT RESISTANCES IN THE FORMATION
AND REMEDIATION OF HYDRATE PLUGS

by

Simon R. Davies
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemical Engineering).

Golden, Colorado
Date 09/04/09

Signed:  
Simon R. Davies

Approved:  
Dr. E. Dendy Sloan, Jr.
Weaver Distinguished Professor
Thesis Advisor

Approved:  
Dr. Carolyn A. Koh
Associate Professor
Thesis Co-advisor

Golden, Colorado
Date 09/04/09

Dr. James F. Ely
Professor and Head,
Chemical Engineering Department
ABSTRACT

Previous predictions of the hydrate formation rate in oil flowlines required an arbitrary fitting parameter which accounted for the effect of mass and heat transfer resistances to hydrate growth. Droplets were assumed to convert directly to hydrate particles at a rate proportional to the thermal driving force and water-hydrocarbon surface area. In order to provide a suitable match to the measured hydrate formation rates in two industrial flowloops, the intrinsic kinetics rate constant had to be reduced by a factor of 500. The rate constant is not transferable to laboratory scale measurements and there is some concern about how transferable the model will be to industrial scale flowlines.

To address these concerns, a revised model is proposed which is based on the mass and heat transfer resistances to hydrate formation. Upon nucleation, a hydrate shell is assumed to form rapidly around the water droplets and further growth is limited by either the transport of hydrate formers across the shell or by heat removal from the hydrate particle. The most sensitive parameters in the model are shown to be the droplet size and the effective diffusivity of the hydrate formers in the hydrate shell. The model is shown to perform reasonably against industrial flowloop data using literature values for the effective diffusivity. Applying the model to industrial scale systems shows that the hydrate formation rate is initially heat transfer limited but becomes increasingly mass transfer limited as the hydrate shells thicken.

In the literature there is some debate about whether the guest or the host molecule is the most mobile within a hydrate shell. This question has important implications for determining the driving force for hydrate formation in a mass trans-
fer limited regime. Mechanistic studies using confocal Raman spectroscopy and high pressure Differential Scanning Calorimetry revealed that water is more mobile than the guest within a methane hydrate film. The studies also revealed that the mass transfer resistance across a hydrate film increases over time as pores are filled.

If hydrate plugs form, they are typically remediated by depressurization. However, in some deepwater fields this is not practical due to the large head of liquid. An alternative technique for plug remediation is to heat the hydrate plug above the hydrate equilibrium temperature. In this work, a heat transfer model for hydrate plug remediation is proposed and validated experimentally. Finally, the hydrate plug remediation model is adapted to predict the extent of dissociation of natural hydrate core samples as they are recovered in three different pressure conditions.
TABLE OF CONTENTS

ABSTRACT ................................................................. iii

LIST OF FIGURES ....................................................... ix

LIST OF TABLES ........................................................ xix

ACKNOWLEDGMENTS ............................................... xx

Chapter 1  INTRODUCTION ........................................ 1

  1.1 An Outline of this Thesis ........................................ 3
  1.2 Publications Arising from this Thesis ....................... 6

Chapter 2  A KINETIC MODEL FOR HYDRATE FORMATION ... 9

  2.1 A Description of the Kinetic Model .......................... 10
  2.2 Parametric Analysis on a Simple Pipe Geometry .......... 12
  2.3 The Application of the Model to Cold Earth Restart of a Well . 16
  2.4 Comparing the Predictions of the Model against Field Data . 21
      2.4.1 Overview of the Field Tests ....................... 22
      2.4.2 Modeling Approach ................................. 22
      2.4.3 Simulation Results .................................. 31
  2.5 Conclusions ...................................................... 38

Chapter 3  INCORPORATING THE TRANSPORT RESISTANCES TO HYDRATE FORMATION ...... 39

  3.1 The Physical Basis of the Transport Model for Hydrate Formation . 39
  3.1.1 External Transport Resistances in the Inertial Subrange .... 41
  3.1.2 External Transport Resistances in the Viscous Subrange .... 44
  3.1.3 Internal Transport Resistances ............................ 48
  3.2 A Sensitivity Analysis on the Transport Model .......... 51
  3.3 The Integration of the Transport Model into OLGA .......... 53
      3.3.1 Inputs and Outputs .................................. 53
      3.3.2 Lookup Tables ...................................... 54
      3.3.3 Tracer Tracking ..................................... 55
Chapter 7  MODELING HYDRATE FORMATION IN INDUSTRIAL FLOWLOOPs, FLOW WHEELS AND STIRRED VESSELS

7.1 Comparing the Model Predictions with Existing Data from a High Pressure Stirred Vessel
7.2 Comparing the Model Predictions with Industrial Flowloop Data
  7.2.1 Experiments at the ExxonMobil Flowloop
  7.2.2 Experiments at the University of Tulsa Flowloop
7.3 Modeling and Analysis Methods
  7.3.1 Results from the Flowloop Experiments
  7.3.2 Results from the ExxonMobil Flowloop Experiments and Simulations
  7.3.3 Results from the Tulsa University Flowloop Experiments and Simulations
7.4 Conclusions

Chapter 8  INDUSTRIAL APPLICATIONS

8.1 Predicting Hydrate Plug Formation in a Subsea Tieback
8.2 Applying the Model to the CONWHYP Stabilized Flow Process
8.3 Conclusions

Chapter 9  HYDRATE PLUG DISSOCIATION

9.1 Previous Studies of the Hydrate Plug Dissociation
9.2 Hydrate Plug Dissociation by Electrical Heating
  9.2.1 Electrical Heating Experimental Procedures
  9.2.2 Electrical Heating Model for Plug Remediation
  9.2.3 Results from the Electrical Heating Experiments
9.3 Predicting Hydrate Dissociation During Core Recovery
  9.3.1 Experimental Setup and Procedures
  9.3.2 Modifications of the Model for Core Recovery
  9.3.3 Results from the Core Recovery Experiments
9.4 Conclusions

Chapter 10 SUMMARY OF CONCLUSIONS

Chapter 11 RECOMMENDATIONS
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>REFERENCES</td>
<td>251</td>
</tr>
<tr>
<td>APPENDIX A INPUTS AND OUTPUTS FOR CSMHYK FROM OLGA</td>
<td>271</td>
</tr>
<tr>
<td>APPENDIX B ACCOUNTING FOR DROPLET CURVATURE</td>
<td>275</td>
</tr>
<tr>
<td>APPENDIX C FOURIER SOLUTION FOR THE DISSOLVED METHANE CONCENTRATION</td>
<td>279</td>
</tr>
<tr>
<td>APPENDIX D DETERMINING THE MASS OF HYDRATE FORMED FROM DISSOLVED METHANE</td>
<td>285</td>
</tr>
<tr>
<td>APPENDIX E CALCULATING THE FRACTIONAL CONVERSION OF ICE TO HYDRATE</td>
<td>287</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

2.1 The Integration of the CSMHyK Kinetic Model into OLGA ....... 13
2.2 Hydrate Formation in an 8 Inch Diameter Pipe 2 Hours After the Restart 14
2.3 Hydrate Formation in a 2 Inch Diameter Pipe 0.5 Hours After the Restart 15
2.4 A Schematic Diagram of the Well that was Simulated ............. 17
2.5 A Pressure Temperature Plot Showing the Hydrate Equilibrium Line for Various Methanol Concentrations and the Well Pressure-Temperature Profile Following the Shut-in ......................... 18
2.6 Pressure Temperature Plots Showing the Hydrate Equilibrium Line and the Well Conditions at Various Times after Restart for 0, 10, 20 and 30 wt% Methanol ......................................................... 19
2.7 A Profile Plot from the CSMHyK – OLGA Simulation Showing the Viscosity Ratio in the Uninhibited Well for 0, 10, 20 and 30 wt% Methanol ................................................................. 20
2.8 A Schematic Representation of the Tommeliten Subsea Tieback to the Edda Platform (See Austvik et al. 1997) ...................... 24
2.9 The Approximate Topography of the Tommeliten Service Line .... 25
2.10 The Effect of the Choke Diameter on the Gas Flow Rate ........ 27
2.11 The Effect of the Productivity Index on the Riser Pressure ....... 28
2.12 The Effect of the Heat Transfer Coefficient on the Riser Temperature 29
2.13 Temperature Profile in the Tieback (left) and Liquid Holdup in the Tieback (right) under Steady State Conditions ................. 31
2.14 A Profile Plot for the Service Line at 5.5 Hours with a slip factor of 0 (left) and a Profile Plot for the Service Line at 5.5 Hours with a Slip Factor of 0.1 (right) for Experiment 4 ......................... 33
2.15 Temperature and Liquid Holdup Profile of the Service Line at 5.5 Hours with a Slip Factor of 0 for Experiment 4 ................................................. 33

2.16 A Profile Plot for the Riser at 1.3 Hours (left) and a Profile Plot for the Service Line at 6.3 Hours (right) for Experiment 5 .......................... 34

2.17 A Profile Plot for the Riser at 0.5 Hours (left) and a Profile Plot for the Service Line at 5 Hours (right) for Experiment 6 ............................. 35

2.18 A Profile Plot for the Service Line at 3 Hours for Experiment 8 . . . 37

3.1 A Conceptual Picture of the Formation of Hydrate Particles in a Pipeline (Turner 2005) ................................................................................................. 40

3.2 A Conceptual Picture of the Conversion of an Entrained Water Droplet to a Hydrate Particle (Taylor 2006) .......................................................... 41

3.3 A Conceptual Picture of the Mass and Heat Transfer Resistances to Hydrate Formation from an Entrained Water Droplet .......................... 42

3.4 The Experimental Data of Laufer (1952) Showing the Variation of the ratio of the Fluctuating Component of the Velocity to the Frictional Velocity against the Radial Position ......................................................... 45

3.5 A Plot Showing the Effect of Peclet Number on the Predicted Sherwood Number Using the Correlations Presented in Equations 3.7 and 3.8 with a Linear Interpolation for the Transition Range ............................. 46

3.6 A Sensitivity Analysis on the Key Parameters in the Transport Model 52

3.7 A Conceptual Picture Showing the Hypothesized Mechanism for Hydrate Growth in the CONWHY P Stabilized Flow Process (Larsen et al. 2001) ........................................................................................................... 57

3.8 The Differences Between the Conceptual Picture for Hydrate Formation in the Transport Model (left) and the Stabilized Flow Model (right) 58

4.1 A Schematic of the High Pressure DSC Apparatus with High Pressure Panel (rated to 400 bar) and Data Acquisition System (Setaram, 2003) 65

4.2 A Schematic of the High Pressure DSC Cell and Furnace . . . . . . . 66

4.3 An Example Thermogram from a Ramped Nucleation Experiment . . 68

4.4 An Example Thermogram from an Isothermal Nucleation Experiment 69
4.5 Thermograms of Multiple Hydrate Nucleation Experiments Performed at Pressure of 200 bar and a Temperature Ramping Rate of 0.5°C/min

4.6 A Pressure - Temperature Plot Showing the Temperature Range for Ice and Hydrate Nucleation for Ramped Experiments with Methane at Various Pressures. The Number of Experiments for Each Point is Displayed on the Plot

4.7 Fraction of Samples in which Ice Nucleated During Ramped Experiments for Methane at Various Pressures and Ramping Rates

4.8 Fraction of Samples in which Hydrate Nucleated During Ramped Experiments for Xenon for Various Ramping Rates and Pressures

4.9 Fraction of Samples in which Hydrate Nucleated During Ramped Experiments for Methane at 32 bar

4.10 Fraction of Samples in which Hydrate Nucleated During Ramped Experiments for Methane at 100 bar

4.11 Fraction of Samples in which Hydrate Nucleated During Ramped Experiments for Methane at 200 bar

4.12 Fraction of Samples in which Hydrate Nucleated During Isothermal Experiments for Methane at 150 bar

4.13 Fraction of Samples in which Hydrate Nucleated During Isothermal Experiments for Pure Methane and for a 75 mol% Methane - 25 mol% Ethane Mixture at 150 bar

5.1 A Simplified Layout of a Raman Spectrometer (Strobel, 2007)

5.2 A Schematic of the Experimental Setup for the Gas Replacement Experiments

5.3 A Schematic of the Experimental Setup for the Gas Replacement (Left) and Water Replacement Experiments (Right)

5.4 A Plot Showing the Predicted Equilibrium Aqueous Phase Concentration as a Function of Temperature Before and After Hydrate Formation at 70 bar (Multiflash CPA Association Model)
5.5  Confocal Microscope Images of the Hydrate Film Showing Pore Filling: 
0 Minutes (Top Left), 10 Minutes (Top Right), 20 Minutes (Lower 
Left), 30 Minutes (Lower Right) ................................................................. 96
5.6  Example Raman Spectra 200 μm from the Top of the Hydrate Film 
(Left) and 800 μm from the Top (Right) 3 Hours after the CO₂ Re-
placement ........................................................................................................ 98
5.7  The Peak-Area-Ratio of CO₂ to CH₄ as a Function of Distance from the 
Top of the Hydrate Film for Various Times after the CO₂ Replacement 99
5.8  Example Raman Spectra for the Gas Phase of CD₄ at 4°C and 70 bar 
Showing the Peak Positions Assigned by Bermejo et al. (1977) .... 100
5.9  Example Raman Spectra for the Gas Phase of CHD₃ Compared to CH₄ 
at 4°C and 70 bar Showing the Peak Positions Assigned by Bermejo et 
al. (1977) ........................................................................................................ 102
5.10 Example Raman Spectra for a Mixed Gas Hydrate of CHD₃ and CH₄ 
with Some Vapor Phase Contribution at 4°C and 70 bar ............ 103
5.11 A Calibration Curve Relating the Peak-Area-Ratio of CH₄ to CHD₃ 
to the Mole Fraction of CH₄ in the Vapor Phase at 4°C and 70 bar . 104
5.12 A Calibration Curve Relating the Peak-Area-Ratio of CH₄ to CHD₃ 
to the Mole Fraction of CH₄ in the Hydrate Phase at 4°C and 70 bar 105
5.13 The Mole Fraction of CHD₃ in the Vapor (Left) and the Hydrate 
(Right) as a Function of Distance from the Top of the Hydrate Film for 
Various Times after the Gas Replacement for a Non-Annealed Hydrate 
Film Formed at 4°C and 70 bar ................................................................. 107
5.14 The Mole Fraction of CHD₃ in the Vapor (Left) and the Hydrate 
(Right) as a Function of Distance from the Top of the Hydrate Film for 
Various Times after the Gas Replacement for a Hydrate Film which 
was Formed at 4°C and 70 bar and Annealed for 24 Hours Before the 
Gas Replacement ................................................................. 108
5.15 The Mole Fraction of CHD₃ in the Vapor (Left) and the Hydrate 
(Right) as a Function of Distance from the Top of the Hydrate Film for 
Various Times after the Gas Replacement for a Hydrate Film which 
was Formed at 4°C and 103 bar and Annealed for 24 Hours Before the 
Gas Replacement ................................................................. 109
5.16 The Mole Fraction of CHD₃ in the Vapor (Left) and the Hydrate (Right) as a Function of Distance from the Top of the Hydrate Film for Various Times after the Gas Replacement for a Hydrate Film which was Formed at 4°C and 140 bar and Annealed for 24 Hours Before the Gas Replacement ......................................................... 110

5.17 A Comparison of the Methane sI Hydrate Phase Boundary for H₂O⁵¹⁸ Water Measured by HP-DSC, with the CSMGem Prediction for H₂O⁵¹⁶ Water ................................................................. 111

5.18 The Effect of the Concentration of O⁵¹⁸ on the Lattice Vibration of Ice Ih ................................................................. 113

5.19 The Effect of the Concentration of O⁵¹⁸ on the Lattice Vibration of sI Methane Hydrate at 4°C and 70 bar .................................................. 114

5.20 A Calibration Curve Relating the Lattice Vibration to the Mole Fraction of H₂O⁵¹⁸ in the Hydrate Phase at 4°C and 70 bar .............................. 115

5.21 The Mole Fraction of H₂O⁵¹⁸ in the Hydrate Lattice as a Function of Distance from the Top of the Hydrate Film for Various Times after the Water Replacement for a Hydrate Film which was Formed at 4°C and 70 bar and Annealed for 24 Hours Before the Water Replacement ................................. 116

5.22 A Repeat Experiment Showing The Mole Fraction of H₂O⁵¹⁸ in the Hydrate Lattice as a Function of Distance from the Top of the Hydrate Film for Various Times after the Water Replacement for a Hydrate Film which was Formed at 4°C and 70 bar and Annealed for 24 Hours Before the Water Replacement ................................. 118

5.23 The Expected Concentration of the H₂O⁵¹⁸ in the Hydrate Film as a Function of Time Based on an Effective Diffusivity of 1×10⁻¹⁶ m²/s .................. 119

5.24 The Expected Concentration of the H₂O⁵¹⁸ in the Hydrate Film after 24 Hours as a Function of Effective Diffusivity ................................. 120

6.1 A Schematic of the Experimental Procedure for the Film Growth Measurements ................................................................. 129

6.2 An Example Thermogram for a Film Growth Measurement ................................................................. 129

6.3 A Schematic Showing the Concentration Profile of Dissolved Methane as it Diffuses to the Hydrate Film ................................. 130
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4</td>
<td>Predicted Concentration Profile of Dissolved Methane as a Function of Time After Hydrate Film Formation</td>
<td>134</td>
</tr>
<tr>
<td>6.5</td>
<td>Mass of the Hydrate Film as a Function of Time For Three Different Temperatures with the Predicted Mass of Hydrate Formed from Dissolved Methane Alone</td>
<td>137</td>
</tr>
<tr>
<td>6.6</td>
<td>Mass of the Hydrate Film as a Function of Time when a Thin Layer of Hydrocarbon was Added to the System</td>
<td>138</td>
</tr>
<tr>
<td>6.7</td>
<td>Mass of the Hydrate Film as a Function of Time for sI Hydrate Formed from Pure Methane and sII Formed from a Methane-Ethane Mixture</td>
<td>141</td>
</tr>
<tr>
<td>6.8</td>
<td>Mass of the Hydrate Film as a Function of Time For Three Different Temperatures with the Predicted Mass of Hydrate Formed from Dissolved Methane And Diffusion Through the Hydrate Film</td>
<td>143</td>
</tr>
<tr>
<td>7.1</td>
<td>Comparisons of the Intrinsic Kinetics Model Predictions to the Autoclave Data from the First Experiment by Turner et al. (2009) 400 rpm, 4°C, 43 bar</td>
<td>147</td>
</tr>
<tr>
<td>7.2</td>
<td>Comparisons of the Transport Model Predictions to the Autoclave Data from the First Experiment by Turner et al. (2009) 400 rpm, 4°C, 43 bar</td>
<td>148</td>
</tr>
<tr>
<td>7.3</td>
<td>Comparisons of the Transport Model Predictions to the Autoclave Data from the Second Experiment by Turner et al. (2009) 400 rpm, 4°C, 49 bar</td>
<td>149</td>
</tr>
<tr>
<td>7.4</td>
<td>Comparisons of the Transport Model Predictions to the Autoclave Data from the Third Experiment by Turner et al. (2009) 500 rpm, 4°C, 43 bar</td>
<td>150</td>
</tr>
<tr>
<td>7.5</td>
<td>Comparisons of the Transport Model Predictions to the Autoclave Data from the Fourth Experiment by Turner et al. (2009) 500 rpm, 4°C, 49 bar</td>
<td>151</td>
</tr>
<tr>
<td>7.6</td>
<td>A Schematic Showing the OLGA Representation of a Flowloop</td>
<td>152</td>
</tr>
<tr>
<td>7.7</td>
<td>A Schematic of the ExxonMobil Flowloop: 10 cm in Diameter, 94.5 m in Length</td>
<td>155</td>
</tr>
<tr>
<td>7.8</td>
<td>A Schematic of the Tulsa University Flowloop (Dellecase et al. 2008)</td>
<td>156</td>
</tr>
</tbody>
</table>
7.9  A Plot Showing the Estimated Vapor Phase Concentration as a Function of Time in the ExxonMobil Flowloop for Conroe Crude Oil, 70% Liquid Loading, Pump Speed 900 rpm, Water Cut 37%  

7.10  A Comparison of the Estimated Water Conversions for the Same Experiment But Using Two Different Calculation Techniques: ExxonMobil Flowloop for Conroe Crude Oil, 70% Liquid Loading, Pump Speed 1400 rpm, Water Cut 50%  

7.11  The Probability of Hydrate Nucleation as a Function of Subcooling in the ExxonMobil Flowloop with the Methane-Ethane Gas Mixture  

7.12  A Set of Images from the ExxonMobil Flowloop Sight Glass Showing the Effect of Hydrate Formation and Dissociation on the Appearance of the System  

7.13  Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Conroe Crude Oil: 60% Liquid Loading, 100 mol% Methane, Pump Speed 280 rpm, 35 vol% Water cut  

7.14  Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Conroe Crude Oil: 70% Liquid Loading, 75 mol% Methane 25 mol% Ethane, Pump Speed 900 rpm, 37 vol% Water cut, Cooled to 4°C  

7.15  Comparisons of the CSMHyK-OLGA Predictions to ExxonMobil Flow Loop Data for Conroe Crude Oil: 70% Liquid Loading, 75 mol% Methane 25 mol% Ethane, Pump Speed 1400 rpm, 37 vol% Water Cut, Cooled to 4°C  

7.16  Comparisons of the CSMHyK-OLGA Predictions to ExxonMobil Flow Loop Data for Conroe Crude Oil: 70% Liquid Loading, 75 mol% Methane 25 mol% Ethane, Pump Speed 900 rpm, 37 vol% Water Cut, Cooled to 10°C  

7.17  Comparisons of the CSMHyK-OLGA Predictions to ExxonMobil Flow Loop Data for Conroe Crude Oil: 70% Liquid Loading, 75 mol% Methane 25 mol% Ethane, Pump Speed 1400 rpm, 37 vol% Water Cut, Cooled to 10°C  

7.18  Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Citgo 220 Model Oil: 50% Liquid Loading, Pump Speed 750 rpm, 25 vol% Water Cut, 2.8°C/hr
7.19 Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Buttermilk Crude Oil: 50% Liquid Loading, Pump Speed 750 rpm, 25 vol% Water Cut, 2.8°C/hr .................................................. 172

7.20 Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Caratinga Crude Oil: 50% Liquid Loading, Pump Speed 750 rpm, 25 vol% Water Cut, 2.8°C/hr .................................................. 173

7.21 Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Troika Crude Oil: 50% Liquid Loading, Pump Speed 750 rpm, 25 vol% Water Cut, 2.8°C/hr .................................................. 174

7.22 Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Troika Crude Oil: 50% Liquid Loading, Pump Speed 750 rpm, 50 vol% Water Cut, 2.8°C/hr .................................................. 175

7.23 Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Troika Crude Oil: 50% Liquid Loading, Pump Speed 750 rpm, 25 vol% Water Cut, 22°C/hr .................................................. 176

8.1 A Schematic Diagram of the Subsea Tieback to be Simulated (Boxall, 2009) ................................................................. 180

8.2 An OLGA Representation of the Subsea Tieback (Boxall, 2009) ................................................................. 181

8.3 A Profile Plot Showing Hydrate Formation Becoming Heat Transfer Limited ................................................................. 182

8.4 A Profile Plot Showing Effect of the Effective Diffusivity on the Hydrate Formation Rate ................................................................. 184

8.5 A Profile Plot Showing Effect of the Nucleation Criterion on the Hydrate Formation Rate ................................................................. 185

8.6 A Profile Plot Showing Effect of the Particle Size on the Hydrate Formation Rate ................................................................. 186

8.7 A Profile Plot Showing Effect of the Droplet Size Scaling Factor on the Ratio of the Hydrate Slurry Viscosity Relative to the Oil ................................................................. 187

8.8 A Profile Plot Showing Effect of the Hydrate-Oil Slip Factor on the Hydrate Formation Rate ................................................................. 188
8.9 A Profile Plot Showing Effect of the Interparticle Adhesion Force on the Ratio of the Hydrate Slurry Viscosity Relative to the Oil .... 189

8.10 A Profile Plot Showing the Effect of Salt Accumulation during Hydrate Formation ......................................................... 191

8.11 An OLGA Representation of a Single-Pass Version of the CONWHYP Stabilized Flow Process ............................................ 193

8.12 The Predicted Hydrate Formation Rates in the OLGA Simulation from the Stabilized Flow Model Showing the Effect of Salt Accumulation on the Water Conversion ........................................ 194

8.13 A Comparison of the Predicted Rate of Water Consumption due to Hydrate Formation for the Kinetics and Stabilized Flow Models ... 195

8.14 The Limiting Mechanism for Hydrate Formation in the Cold Flow Model is Shown to be Heat Removal from The Hydrate Particles. The Thickness of the Water Film is Less than One Micron .......... 196

8.15 A Comparison of the Predicted Hydrate Slurry Viscosities With and Without Particle Agglomeration ...................................... 198

8.16 The Effect of Particle Size on the Hydrate Formation Rate ........ 199

8.17 The Effect of Pipe Diameter on the Hydrate Formation Rate ........ 200

8.18 The Effect of the Well Stream Fluid Temperature on the Hydrate Formation Rate ............................................................ 201

8.19 The Effect of the Slurry Flow Rate on the Hydrate Formation Rate for a 20 cm Diameter Pipeline ........................................... 202

8.20 The Effect of the Slurry Flow Rate on the Hydrate Formation Rate for a 30 cm Diameter Pipeline ........................................... 203

8.21 The Effect of the Slurry Flow Rate on the Hydrate Formation Rate for a 50 cm Diameter Pipeline ........................................... 204

8.22 The Effect of the Slurry Flow Rate on the Fluid and Equilibrium Temperatures for a 30 cm Diameter Pipeline ......................... 205

9.1 A Schematic of the Apparatus used for the Electrical Heating Experiments for Highly Permeable Plugs ................................. 213
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2</td>
<td>A Raman Spectra of the sII Hydrate formed from the 65 mol% Methane, 35 mol% Ethane Gas Mixture (Hester, 2004)</td>
</tr>
<tr>
<td>9.3</td>
<td>A Comparison of the Conceptual Pictures for Hydrate Plug Dissociation By: (a) Two-Sided Depressurization (Peters, 1999), (b) One-Sided Depressurization (Bollavaram, 2002), and (c) Electrical Heating</td>
</tr>
<tr>
<td>9.4</td>
<td>The Finite Difference Grid that was Used to Numerically Simulate the Hydrate Plug Dissociation</td>
</tr>
<tr>
<td>9.5</td>
<td>A Comparison of Electrical Heating Experiments and Model Predictions for sI and sII Hydrate</td>
</tr>
<tr>
<td>9.6</td>
<td>A Comparison of Electrical Heating Experiments With and Without Conroe Crude Oil</td>
</tr>
<tr>
<td>9.7</td>
<td>A Comparison of the Pressure Increase During Electrical Heating Experiments in a Closed System With and Without Conroe Crude Oil</td>
</tr>
<tr>
<td>9.8</td>
<td>A Comparison of Electrical Heating Experiments with Even and Uneven Heat Fluxes</td>
</tr>
<tr>
<td>9.9</td>
<td>A Comparison of the Temperature Ramp Achieved in the Laboratory Compared to that Experienced by a Core from ODP Leg 204 (Winters, 2005)</td>
</tr>
<tr>
<td>9.10</td>
<td>The Fits to the Predicted Hydrate Equilibrium Curves that were used in the Core Recovery Model</td>
</tr>
<tr>
<td>9.11</td>
<td>A Conceptual Picture of the Temperature Profile Inside a Dissociating Hydrate-In-Sediment Core Sample</td>
</tr>
<tr>
<td>9.12</td>
<td>The Predicted Composite Thermal Conductivities for the Phase Fractions in Test 1</td>
</tr>
<tr>
<td>9.13</td>
<td>A Comparison of the Predicted and Measured Hydrate Dissociation Rates for Test 2</td>
</tr>
<tr>
<td>9.14</td>
<td>A Comparison of the Predicted and Measured Hydrate Dissociation Rates for Test 3</td>
</tr>
<tr>
<td>9.15</td>
<td>A Comparison of the Predicted and Measured Hydrate Dissociation Rates for Test 4</td>
</tr>
<tr>
<td>B.1</td>
<td>Differential Volume Element on a Sphere from Bird et al. (2002)</td>
</tr>
</tbody>
</table>
LIST OF TABLES

2.1 The Composition of the Tommeliten Gas Condensate .................. 23
2.2 The Hydrate Equilibrium Curve for the Tommeliten Gas Condensate 30
3.1 The Base Case Values for the Sensitivity Analysis .................... 51
6.1 Methane Concentrations in the Aqueous Phase as Estimated by *Multi*\textit{flash} ............................................. 131
6.2 Methane Concentrations in the Aqueous Phase as Estimated by *Multi*\textit{flash} (CPA Assoc.) and *CSM*\textit{Gem} Compared to Experimental Data (Chapoy et al. 2004) ....................................................... 131
7.1 The Chemical Composition of Conroe Crude Oil ...................... 154
7.2 The Chemical Composition of Tulsa City Gas ........................... 157
8.1 The Simulation Matrix for the Sensitivity Analysis .................... 198
9.1 The Default Parameters Used in the *CSMPlug* Program for Industrial Hydrate Plug Dissociation by Electrical Heating .................. 221
9.2 A Comparison of the Experimental Results for Hydrate Plug Dissociation by Electrical Heating Compared to the Model Predictions .... 223
9.3 A List of the Thermal Properties of the Pure Phases that were used in the Model .................................................. 235
9.4 An Experimental Matrix for the Core Recovery Experiments ....... 236
A.1 Original Inputs and Outputs for the Kinetic Model ................... 272
A.2 Additional Input and Outputs for the Transport Model ............... 273
A.3 Additional Input and Outputs for the Tracer Tracking and Cold Flow Models .......................................................... 274
ACKNOWLEDGMENTS

Firstly, I would like to thank my thesis advisers: Professors E. Dendy Sloan and Carolyn A. Koh for their guidance and for the numerous opportunities that they have afforded me over the past 5 years. I would also like to thank Professor Amadeu K. Sum for his involvement on this work. Thanks to my thesis committee: Professors Sumit Agarwal, Matt Liberatore, Mike Walls and Dr. Jeff Creek for their suggestions and for the useful discussions that have shaped the concepts and ideas presented in this thesis.

I would like to gratefully acknowledge the CSM Hydrate Consortium and the Deepstar consortium of energy companies for funding this work and for the frequent comments and feedback that I have received. In particular I would like to thank: Jeff Creek and Alberto Montesi of Chevron for allowing me to work with them for the summer of 2006; Keijo Kinnari, Xiaoyun Li and Pål Hemmingsen of StatoilHydro for sharing the Tommeliten field data and for suggesting the stabilized flow modeling; Larry Talley, Doug Turner and Glenn Cobb of ExxonMobil for allowing us unprecedented access to their flowloop facilities; Mike Volk and Emmanuel Delle-Case of Tulsa University for sharing their flowloop data; Adam Ballard, George Shoup and Norm McMullen of BP for their frequent discussions and suggestions on the plug remediation experiments; and Greg Hatton of Shell for his insight on the physical principles behind our correlations. Thanks to Zheng Gang Xu and Andris Skatebo of SPTGroup for their frequent modifications to OLGA which enabled the much of the new functionality of CSMHyK.

Finally, and perhaps most importantly I would like to thank the members of
the hydrate group past and present for their friendship, advice, support and good humor over the years. I am particularly grateful to John Boxall who has worked with me extensively on $CSMHyK - OLGA$ and helped to pioneer the application of the model to industrial flowloops as described in Chapter 7. Thanks to Keith Hester for answering my numerous questions about gas hydrates and for his important intellectual contributions to Chapter 4. Thanks to Tim Strobel for his numerous suggestions and critiques throughout this work. Thanks to Jason Lachance for his contributions to the DSC experiments. Thanks to Professor Sugahara, Dr. Prasad and Dr. Ohno for their help and advice on Raman spectroscopy. Thanks to Jason Ivanic and Thomas Hughes for helping me get started in the laboratory. Thanks also to the undergraduate researchers that have helped me: Laura Stadterman; Kristin Bowler; Jared Marchildon; Collin Timm; Justin Panter; Nick Shult; Jennifer Gallardo and Trevor Braun.
In memory of my granddad Harold Davies
Chapter 1

INTRODUCTION

Clathrate hydrates are crystalline inclusion compounds that consist of a hydrogen bonded host lattice comprised of water cages which encapsulate small guest molecules at high pressures and low temperatures. When they were first discovered in Birmingham UK by Priestly (1778) from a mixture of SO$_2$ and water, they were mainly studied out of scientific curiosity until Hammerschmidt (1934) discovered that hydrates were a cause of plugging of natural gas transmission lines. Today gas hydrates continue to be the most prevalent flow assurance problem in offshore oil and gas operations: an order of magnitude worse than waxes and two orders of magnitude worse than asphaltenes. In addition to their importance in flow assurance, hydrates have also been discovered in nature (Makogon 1965) where they occur in oceanic sediments and permafrost regions. Natural gas hydrates represent a significant energy resource. Estimates of the amount of gas contained in these natural deposits range from $1 \times 10^{14}$ to $1 \times 10^{15}$ m$^3$ (Milkov 2004).

The two most common types of hydrate structures that form from natural gas/water systems are structure I and structure II. Structure I tends to enclathrate smaller natural gas molecules such as methane, whereas structure II tends to enclathrate larger natural gas molecules such as propane (Sloan and Koh, 2008). The most common naturally occurring hydrate structure is structure I whereas structure II hydrates tend to form in oil and gas flow lines. The thermodynamic conditions that are favorable for hydrate formation are now well understood (Ballard, 2003).
As the oil and gas industry moves into deeper water, the risk of hydrate plugging increases due to the higher pressures exerted by the additional liquid head, and due to the longer tiebacks in which the production fluids cool deep into the hydrate stability zone. In addition, the consequences of forming a hydrate plug in deeper water are more severe; it is often not possible to remove the hydrate plug by venting alone and other more novel methods are required. Concurrently, as oil and gas resources are depleted, less economic fields are being developed; the economics of these marginal field developments can be improved by reducing the requirements for chemical additives. This has necessitated a change in strategy away from the traditional approach of avoiding the thermodynamically favorable conditions for hydrate formation using inhibitors, towards a risk management approach where pipelines are deliberately operated under conditions where hydrates are thermodynamically stable.

One example of a risk management approach to hydrate formation is the use of low dosage hydrate inhibitors (LDHIs) such as kinetic inhibitors and antiagglomerants. Kinetic inhibitors delay the formation of hydrate, whereas anti-agglomerants prevent hydrate particles adhering to one another (Kelland, 2006). Another example of risk management is cold or stabilized flow (Gudmundsson, 2002) where hydrate particles are deliberately formed under conditions selected to avoid agglomeration and plugging. The key to a successful risk management strategy is an understanding of the timescales required for hydrate plug formation and remediation.

A conceptual picture for hydrate formation in oil pipelines was presented by Turner (2005). Water droplets are entrained into the oil phase and upon nucleation a hydrate film then forms rapidly around the water droplets. Once the hydrate film has formed, further hydrate formation is limited by mass transfer of the guest and host molecules across the hydrate film. These hydrate particles can later agglomerate
to form a hydrate plug.

The Colorado School of Mines has been developing a model for hydrate plug formation since 2003. The rate of hydrate formation in early generations of the model (Boxall et al. 2008 a) was calculated using a chemical kinetics equation based on the temperature driving force for hydrate formation. An adjustable parameter that had been regressed to data from one industrial flowloop was used to account for the mass and heat transfer resistances in a second flowloop for four different oils. However, without a sound physical interpretation of the driving force for hydrate formation and the kinetic rate constant, scaling up the model to industrial systems may prove problematic.

1.1 An Outline of this Thesis

The aim of this thesis is to apply chemical engineering principles to the problem of hydrate plug formation and remediation in order to provide the practicing petroleum engineer with reliable predictive tools to support a risk-management approach to hydrate plug formation. This chapter aims to provide the reader with an overview of the work performed and to highlight some of the most important findings from this thesis.

Chapter 2 of this thesis demonstrates how the kinetics model (Boxall et al. 2008 a) can be applied to predict the rate of hydrate plug formation in industrial systems using the Tommeliten field trials as an example. The predicted rate of hydrate formation in industrial systems was often limited by the rate of heat removal from the pipeline for both oil and gas systems, hence the model can be used to provide a worst-case prediction for the amount of hydrate formed in such systems (Montesi, 2005). For the Tommeliten field trials, a gas-condensate field, the model was found
to give the correct order of magnitude of the timescale of hydrate plug formation without any adjustments for mass or heat transfer resistances within the flow line. However, the predicted location of the plug was not accurate.

Although the chemical kinetics model can be used to give a worst case estimate for the hydrate formation rate in industrial systems, a more accurate prediction would require a better understanding of the mass and heat transfer resistances and how these resistances scale between the laboratory and the flow line. In order to address this problem, a study was initiated into the mass and heat transfer resistances to hydrate formation in oil dominated systems. In Chapter 3, a revised hydrate formation model is presented based on the conceptual picture of Turner (2005). The most sensitive parameters in the model are shown to be the diameter of the entrained water droplets and the effective diffusivity of the guest and host molecules across the hydrate shell.

A key component of any hydrate formation model is the nucleation criterion. Hydrate nucleation is a stochastic process, but in the hydrate formation model a nucleation criterion of 6.5°F (3.6°C) was chosen based on a rule-of-thumb by Matthews et al. (2000). Chapter 4 describes a set of experiments that was performed in order to better understand the variables that affect hydrate nucleation.

Once a hydrate shell grows around an entrained water droplet, further hydrate formation is limited by the rate of mass transfer of host and guest molecules across the shell. However, there is some controversy about whether it is the transport of the guest (Makogon 1981; Teng et al. 1996; Hirai et al. 1996; Henning et al. 2000; Wang et al. 2002; Moudrakovski et al. 2004), or the host molecule (Topham et al. 1984; Shindo et al. 1995; Mori and Mochizuki 1996; Sugaya and Mori 1996; Mori and Mochizuki 1997; Mochizuki and Mori 2000) across the film that controls the hydrate growth. This question has two important implications for flow assurance: first it will
affect the mass transfer driving force; second if the outer surface of partially converted hydrate particles is covered by a thin layer of water then the particles would have a higher tendency to agglomerate (Taylor, 2006). The Raman spectroscopy results that are presented in Chapter 5 suggest that water is the most mobile species in a hydrate film.

In Chapter 6, Differential Scanning Calorimetry experiments on hydrate film growth are described. These experiments aimed to better quantify the mass transfer rate across a hydrate shell. Subsequent modeling of the hydrate film growth rates revealed some interesting annealing behavior.

A key test of the reliability of the mass and heat transfer model described in Chapter 3 and refined in the subsequent chapters, is its ability to predict the rate of hydrate formation in industrial flowloops. Chapter 7 describes the work that was performed to test the model against flowloop data from the ExxonMobil Upstream Research Company and from Tulsa University.

The industrial applications of the new model for hydrate formation are demonstrated in Chapter 8 through case studies. Modifications to the model facilitated its application to systems containing thermodynamic inhibitors whose accumulation would lead to less favorable conditions for hydrate formation as more of the water converts to hydrate. The model was also adapted to predict the hydrate formation rate in stabilized flow systems where water droplets coat the outer surface of pre-existing hydrate particles before converting to hydrate.

Finally, experiments and modeling of novel hydrate plug remediation strategies are described in Chapter 9. These strategies would find application in some deepwater field developments where depressurization alone will be insufficient to bring a plug out of the hydrate stability region due to the large residual head of liquid present
The following refereed publications resulted directly from this thesis work:


The following publications in conference proceedings resulted from this thesis work:


Chapter 2

A KINETIC MODEL FOR HYDRATE FORMATION

The cost of thermodynamically inhibiting subsea tiebacks under steady state and transient operations can be prohibitive and it is often not possible for the flow assurance engineer to avoid the hydrate stability zone in all foreseeable operating scenarios. Instead, a risk management approach is often adopted to prevent hydrate plug formation (Kinnari et al. 2008, Pausche et al. 2002). Due to the potentially severe economic impact of forming a hydrate plug, it is critical to accurately assess the risk of hydrate plug formation for a new field design or restart procedure. Predictions of hydrate growth rates are a key component of this risk assessment.

A number of models have been proposed for hydrate growth rates in laboratory scale systems. The models are either based on chemical kinetics equations (Vysniauskas and Bishnoi 1983, Englezos et al. 1987, Christiansen and Sloan 1995, Lee et al. 2005) or on interfacial mass transfer resistances to hydrate formation (Skovborg and Rasmussen 1994). The applicability of these models is generally limited to apparatus of a similar geometry to the apparatus in which the measurements were taken due to the inherent difficulties in scaling the models to alternative geometries.

Since 2003, the Colorado School of Mines has been developing a model for hydrate formation in industrial scale flow lines in conjunction with SPTGroup. The model, \textit{CSMHyK version} 1.0, is incorporated as a plug-in module in the transient multiphase flow simulator, \textit{OLGA} (Turner et al. 2005). \textit{CSMHyK} was initially developed for oil flow lines, but has also proven to be a valuable tool for Chevron when
making design decisions for new field developments (Montesi, 2005). The model is based on intrinsic chemical kinetics; the problem of scaling the predictions to industrial scale systems is overcome by regressing the kinetic constants to the growth rate measured in an industrial scale flowloop for one oil and then comparing the predictions to the measured growth rate in a second flowloop of similar geometry for four different oils. Good agreement was obtained between the predictions and the flowloop data (Boxall, 2009).

Recently, an alternative model for hydrate formation in industrial systems has been developed by Calsep. The model, Flowasta, is based on mass transfer rates between the hydrocarbon liquid and the water phase. The model currently relies on fitted parameters for the mass transfer resistances and work is in progress to validate the model against industrial scale flowloops. At the time of writing, Flowasta was available only in a proprietary beta version and not available for use in this thesis.

This chapter is divided into five sections. Section 2.1 contains a description of CSMHyK version 1.0. Section 2.2 describes a parametric analysis on the restart of a simple pipe geometry. The remaining sections discuss the applications and the limitations of the model for industrial systems. Two industrial applications are highlighted:

- **Section 2.3:** The application of the model to cold earth restart of a well.
- **Section 2.4:** A comparison of the model against field data.

### 2.1 A Description of the Kinetic Model

CSMHyK is a plug-in module for the OLGA multiphase flow simulator. The model predicts the rate of hydrate formation using a first-order rate equation based
on the thermal driving force. The kinetic rate equation was originally proposed by Vysniauskas and Bishnoi (1983) based on a fugacity driving force and in the absence of mass and heat transfer limitations. The fugacity driving force was replaced with a more convenient thermal driving force $\Delta T$, as described by Turner et al (2005). The revised form of the kinetic equation is given in Equation 2.1 where $m_{gas}$ is the mass of gas consumed during hydrate formation, $k_1$ and $k_2$ are the intrinsic rate constants and $T$ is the absolute temperature. As water droplets convert to hydrate particles, the surface area available for hydrate formation, $a_s$, decreases, slowing down the rate of hydrate formation.

$$\frac{dm_{gas}}{dt} = -uk_1e^{-\frac{k_2}{T}}a_s\Delta T$$  

(2.1)

In order to accurately simulate hydrate formation in flowloops, it was necessary to reduce the intrinsic kinetic rate constant by a factor of 500 (Boxall et al. 2008 b). This lumped parameter $u$ accounts for mass and heat transfer limitations in the flowloops. The value of the constants $k_1$ and $k_2$ for sII hydrate are $2.55 \times 10^{16}$ kg/m$^2$/s/K and 13600 K, respectively (Turner et al. 2005).

The kinetic model assumes that water droplets convert completely into hydrate particles. Nucleation is assumed to occur instantaneously at a subcooling of 6.5°F (3.6°C), as suggested by Matthews et al. (2000). Once formed, the model assumes that these particles remain in the oil phase and are transported at a velocity proportional to the oil phase velocity. The proportionality constant $C_{OIL}$, is adjustable between 0 and 1, the default being 1 where the hydrate and oil velocities are equal.

The change in the relative viscosity of the oil phase $\mu_r$, is then found from the Mills Equation (Mills et al. 1985) as shown in Equation 2.2 using a maximum packing fraction of particles ($\Phi_{max}$) of 4/7, and the effective volume fraction of the hydrate
agglomerates $\Phi_{eff}$ (Equation 2.3). $\Phi_{eff}$ is in turn found from the Camargo and Palermo (2002) correlation for steady state flow as stated by Equation 2.4, where $d_p$ and $d_A$ are the monomer and aggregate diameters respectively, $F_a$ is the interparticle adhesion force, $\dot{\gamma}$ is the volume averaged shear rate, $f$ is the fractal dimension of the aggregates, $\mu_0$ is the viscosity of the crude oil and $\Phi$ is the volume fraction of hydrate. An overview of the current CSMHyK module and its integration into OLGA is shown in Figure 2.1.

$$\mu_r = \frac{1 - \Phi_{eff}}{1 - \Phi_{max}}$$  \hspace{1cm} (2.2)

$$\Phi_{eff} = \Phi \left(\frac{d_A}{d_p}\right)^{3-f}$$  \hspace{1cm} (2.3)

$$\left(\frac{d_A}{d_p}\right)^{4-f} - \frac{F_a(1 - \Phi_{max} \left(\frac{d_A}{d_p}\right)^{3-f})^2}{d_p^2 \mu_0 \dot{\gamma} \left[1 - \Phi \left(\frac{d_A}{d_p}\right)^{3-f}\right] \mu_0 \dot{\gamma}} = 0$$  \hspace{1cm} (2.4)

### 2.2 Parametric Analysis on a Simple Pipe Geometry

In order to elucidate the most sensitive parameters in the model and the limiting mechanisms for hydrate formation, a simple pipe geometry 10 kilometers in length was simulated for a variety of restart conditions. The pipeline was initially empty and an oil phase with a gas to oil ratio (GOR) of 280 sm$^3$/sm$^3$, a water cut of 30 vol%, and a stock tank density of 0.7756 g/cm$^3$ (API gravity of 51°), was introduced from one end at a temperature of 27°C. The downstream pressure was set to 1500 psia (103 bara). The external heat transfer model was defined as sea water with a velocity of 0.32 m/s and a temperature of 4°C.
The effect of pipeline diameter on the limiting mechanism for hydrate formation was investigated. The Nusselt number for the interior of the pipeline was held constant for all cases to ensure the heat transfer effects were comparable between cases. The simulations indicated that hydrate formation in pipelines with larger diameters was limited by the rate of heat removal from the pipeline (See Figure 2.2), whereas the formation rate for smaller diameter pipelines proceeded to completion, limited by the availability of water (See Figure 2.3). This effect is attributed to the higher surface to volume ratio for smaller diameter pipelines which increases the heat transfer rate. Similar results were derived from simulations repeated for a constant Reynolds number.
Figure 2.2. Hydrate Formation in an 8 Inch Diameter Pipe 2 Hours After the Restart
Figure 2.3. Hydrate Formation in a 2 Inch Diameter Pipe 0.5 Hours After the Restart
2.3 The Application of the Model to Cold Earth Restart of a Well

The kinetic model was used to simulate the restart of a vertical well which had been shut-in for five days. The parameters in the well simulation were selection after correspondence with Creek (2006) of Chevron to ensure industrial relevance. The oil had a GOR of 424 sm$^3$/sm$^3$, a stock tank density of 0.839 g/cm$^3$ (API gravity of 37°), and a water cut of 35 vol%. A schematic representation of the well is shown in Figure 2.4. The water depth was 518 m and the base of the well was located 1525 m below the mud line. The reservoir conditions in the simulation were 115°C and 345 bar. The simulations were performed in three parts in order to ensure that a representative fluid distribution and temperature profile were obtained prior to restart:

1. Establish steady state operation for five days

2. Shut-in the well for five days

3. Add the $CSMHyK$ module and restart the well

The simulated temperature-pressure profile of the well at the end of the five day shut-in is shown in Figure 2.5. The hydrate equilibrium curves for various concentrations of methanol are plotted on the same figure. The figure shows that even 30 wt % of methanol is insufficient to fully thermodynamically inhibit the well, since hydrates are still stable at the pressure and temperature conditions in the well by the mud line. Even though 30 wt% of methanol is insufficient to fully thermodynamically inhibit the well following the shut-in, it is possible that the line will be kinetically inhibited, i.e. there will be insufficient time and / or subcooling to form enough hydrate to plug the well. This is the main advantage of a time-dependent hydrate
Figure 2.4. A Schematic Diagram of the Well that was Simulated
Figure 2.5. A Pressure Temperature Plot Showing the Hydrate Equilibrium Line for Various Methanol Concentrations and the Well Pressure-Temperature Profile Following the Shut-in

formation model incorporated into a transient multiphase flow simulator compared to steady-state thermodynamic models.

For the restart simulations, the default subcooling criterion of 6.5°F (3.6°C) was used. An hydrate-oil slip ratio of zero was chosen to avoid the hydrate being transported out of the well by the oil phase. Intrinsic growth kinetics were used, i.e. with no mass or heat transfer limitations.

The results from the restart simulations are shown in Figure 2.6 for methanol concentrations of 0, 10, 20 and 30 wt%. In each case the pressure-temperature profile started off partially inside the hydrate stability region. In the uninhibited case, the
Figure 2.6. Pressure Temperature Plots Showing the Hydrate Equilibrium Line and the Well Conditions at Various Times after Restart for 0, 10, 20 and 30 wt% Methanol accumulation of hydrate in the well caused a significant reduction in the oil and gas flow rates, this meant that warm reservoir fluids took longer to reach the hydrate and dissociate it. After 30 minutes the well was still deep inside the hydrate formation region. With 30 wt% of methanol, the well was in the hydrate formation region for less than five minutes, and the maximum subcooling was just 5°F (2.8°C) which did not satisfy the nucleation criterion.

Profile plots for the well in the four simulations are shown in Figure 2.7. The most severe flow impedance occurred in the uninhibited case as indicated by the low flow rates of the oil and gas phases. No hydrate formed in the simulation with 30 wt% of methanol.
Figure 2.7. A Profile Plot from the CSMHyK – OLGA Simulation Showing the Viscosity Ratio in the Uninhibited Well for 0, 10, 20 and 30 wt% Methanol
With a hydrate-oil slip factor $C_{oil}$, of zero, $CSMHyK – OLGA$ predicted the formation of a hydrate plug in an industrial system. A plug was indicated by a spike in the viscosity ratio (the slurry viscosity/the oil viscosity). The model predicted that under certain conditions, the plugging of a well may not occur during restart even though hydrates would be thermodynamically stable. Field verification for the current model is limited; recent attempts to model the Tommeliten field will be discussed in the following section.

2.4 Comparing the Predictions of the Model against Field Data

Predictions from the kinetic model were compared to field data from Statoil-Hydro on hydrate plug formation in the Tommeliten gas condensate field. The gas condensate had a GOR of 622 sm$^3$/sm$^3$, the condensate had a stock tank density of 0.842 g/cm$^3$ (API gravity of 37$^\circ$), and a water cut of 9.5 vol%. Field data was available for four typical operating scenarios: 1. steady state operation with failure of inhibitor injection, 2. restart of an uninhibited line, 3. restart of an under-inhibited line and 4. restart of a depressurized line.

Although the $CSMHyK$ model was designed for oil flow lines, the model was able to predict the correct timescale for hydrate plug formation in this gas condensate tieback, provided that mass and heat transfer resistances within the pipeline were neglected and the hydrate-oil slip velocity was set to zero. The predicted locations of the plugs were further upstream than observed in the field trials. This was a result of the hydrate-oil slip factor being zero, which forced the hydrate to accumulate where it initially formed. In reality, hydrate agglomerates could be carried further downstream before eventually jamming in dips.
2.4.1 Overview of the Field Tests

A simplified schematic of the Tommeliten tieback to the Edda platform is shown in Figure 2.8. The composition of the Tommeliten gas condensate is given in Table 2.1. The tieback consisted of two production lines, each 0.23 meters (9 inches) in diameter and a 0.15 meter (6 inch) diameter uninsulated service line. The hydrate experiments were all carried out in the service line. The service line passed over several other pipelines between the subsea wellhead and the Edda platform. The other pipelines created additional dip sections in which hydrate chunks could potentially jam. In the experiments, the hydrate plugs consistently formed in the same subsea location, as indicated in Figure 2.9. The service line was produced into the test separator on the Edda platform via a choke valve on the topsides. The following data were recorded during the field tests: the methanol injection rate; the temperature and pressures in the well bore, service line riser and test separator; gamma ray densitometer readings of the riser topside; the choke valve position; the water and oil levels in the test separator; the mass flow rates from test separator of oil, water and gas.

Hydrate plugs formed subsea in four of the eight experiments. Experiment 4 was performed to emulate the restart of a depressurized line. Experiment 5 was a steady-state operation with induced methanol-injection failure. In Experiment 6, an initially pressurized line was restarted after a 16-hour shut-in with uninhibited fluids. In Experiment 8, a pressurized line was restarted after a 23-hour shut-in with underinhibited fluids.

2.4.2 Modeling Approach

The fluid property tables for the OLGA simulations were constructed in Multi flash using the RKSAdvanced equation-of-state. According to Austvik (1995), condensate
Table 2.1. The Composition of the Tommeliten Gas Condensate

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol. %</th>
<th>Mol. wt. (g/mol.)</th>
<th>Liquid Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>2.271</td>
<td>18.015</td>
<td>0.999</td>
</tr>
<tr>
<td>N₂</td>
<td>0.177</td>
<td>28.014</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>2.977</td>
<td>44.01</td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>79.206</td>
<td>16.043</td>
<td></td>
</tr>
<tr>
<td>C₂</td>
<td>7.271</td>
<td>30.07</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>2.867</td>
<td>44.097</td>
<td></td>
</tr>
<tr>
<td>iC₄</td>
<td>0.524</td>
<td>58.124</td>
<td></td>
</tr>
<tr>
<td>nC₄</td>
<td>1.022</td>
<td>58.124</td>
<td></td>
</tr>
<tr>
<td>iC₅</td>
<td>0.384</td>
<td>72.151</td>
<td></td>
</tr>
<tr>
<td>nC₅</td>
<td>0.435</td>
<td>72.151</td>
<td></td>
</tr>
<tr>
<td>C₆</td>
<td>0.69</td>
<td>86.178</td>
<td>0.664</td>
</tr>
<tr>
<td>C₇</td>
<td>0.473</td>
<td>99.6</td>
<td>0.717</td>
</tr>
<tr>
<td>C₈</td>
<td>0.546</td>
<td>106.6</td>
<td>0.747</td>
</tr>
<tr>
<td>C₉</td>
<td>0.408</td>
<td>119.5</td>
<td>0.766</td>
</tr>
<tr>
<td>C₁₀</td>
<td>0.252</td>
<td>135.5</td>
<td>0.773</td>
</tr>
<tr>
<td>C₁₁</td>
<td>0.162</td>
<td>154.4</td>
<td>0.774</td>
</tr>
<tr>
<td>C₁₂</td>
<td>0.085</td>
<td>170.7</td>
<td>0.785</td>
</tr>
<tr>
<td>C₁₃</td>
<td>0.08</td>
<td>183.7</td>
<td>0.796</td>
</tr>
<tr>
<td>C₁₄</td>
<td>0.052</td>
<td>197.7</td>
<td>0.81</td>
</tr>
<tr>
<td>C₁₅</td>
<td>0.038</td>
<td>210.9</td>
<td>0.813</td>
</tr>
<tr>
<td>C₁₆</td>
<td>0.024</td>
<td>226.3</td>
<td>0.82</td>
</tr>
<tr>
<td>C₁₇</td>
<td>0.018</td>
<td>243.6</td>
<td>0.822</td>
</tr>
<tr>
<td>C₁₈</td>
<td>0.013</td>
<td>259.3</td>
<td>0.83</td>
</tr>
<tr>
<td>C₁₉</td>
<td>0.004</td>
<td>270.5</td>
<td>0.837</td>
</tr>
<tr>
<td>C₂₀</td>
<td>0.021</td>
<td>412.4</td>
<td>0.876</td>
</tr>
</tbody>
</table>
and water mass fractions leaving the separator are 16 and 2 wt% respectively, which compared well to the *Multiflash* predictions for the fluid composition at the separator conditions of 19 and 1.7 wt% respectively.

In order to establish a representative *OLGA* model of the Tommeliten tieback to which the *CSMHyK* model could be added, three unknown parameters were regressed to data from an earlier experiment before hydrate formation. The three parameters were: the production index of the well which is the proportionality constant relating the flow rate from the well to the pressure driving force, the heat transfer coefficient of the pipeline, and the orifice size of the choke valve.

First, the reservoir and separator pressures and temperatures were fixed in the *OLGA* model; these parameters were reported by *StatoilHydro* (Berge et al. 1994). Next a series of simulations were performed in which the riser pressure was set to the experimentally recorded value. The choke valve orifice size was adjusted until
Figure 2.9. The Approximate Topography of the Tommeliten Service Line
the mass flow rate of gas matched the measured values (Figure 2.10). Once the orifice size had been fixed, the Productivity Index in the well model was adjusted so as to match the riser pressure (Figure 2.11). Finally, the heat transfer coefficient from the service line was adjusted to match the riser temperature (Figure 2.12). The procedure was iterative since all three parameters were interacting; three iterations were required to optimize the three parameters. The optimal values of the parameters were: an orifice diameter of 2.8 cm, a productivity index of $2.5 \times 10^{-6}$ kg/s/Pa and a heat transfer coefficient of 6.8 W/m²/K. Once the parameters had been optimized to steady state data, the $CSMHyK$ module was added to the $OLGA$ model. The hydrate equilibrium P-T curve was found for the fluid composition using $CSMGem$ (Ballard and Sloan 2002, Sloan and Koh 2008) and is shown in Table 2.2. The initial liquid loadings were found from simulations of steady state operation, the initial pressures and temperatures for each experiment were reported by Berge et al. (1994).

In these simulations, hydrates were allowed to form according to intrinsic kinetics with no mass or internal heat transfer limitations, this corresponded to a value of unity for the lumped parameter, $u$, in Equation 2.1. The water droplets were fully entrained in the condensate phase and hydrate nucleation was set to occur instantaneously once a 3.6°C (6.5°F) subcooling was attained. Once nucleated, the hydrate was forced to accumulate where it initially formed by setting the hydrate-oil slip factor $COIL$ in $OLGA$ to zero. A hydrate plug was inferred from the oil viscosity ratio (slurry viscosity / oil viscosity) and the pressure drop.
Figure 2.10. The Effect of the Choke Diameter on the Gas Flow Rate
Figure 2.11. The Effect of the Productivity Index on the Riser Pressure
Figure 2.12. The Effect of the Heat Transfer Coefficient on the Riser Temperature
Table 2.2. The Hydrate Equilibrium Curve for the Tommeliten Gas Condensate

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.939</td>
<td>-27.9</td>
</tr>
<tr>
<td>2.57</td>
<td>-15.5</td>
</tr>
<tr>
<td>5.21</td>
<td>-3.14</td>
</tr>
<tr>
<td>6.00</td>
<td>-0.346</td>
</tr>
<tr>
<td>6.06</td>
<td>-0.129</td>
</tr>
<tr>
<td>6.20</td>
<td>0.0377</td>
</tr>
<tr>
<td>7.05</td>
<td>0.909</td>
</tr>
<tr>
<td>17.0</td>
<td>7.38</td>
</tr>
<tr>
<td>38.3</td>
<td>13.5</td>
</tr>
<tr>
<td>55.6</td>
<td>16.2</td>
</tr>
<tr>
<td>72.1</td>
<td>17.8</td>
</tr>
<tr>
<td>88.2</td>
<td>19.0</td>
</tr>
<tr>
<td>104</td>
<td>19.9</td>
</tr>
<tr>
<td>120</td>
<td>20.6</td>
</tr>
<tr>
<td>136</td>
<td>21.2</td>
</tr>
<tr>
<td>151</td>
<td>21.7</td>
</tr>
<tr>
<td>167</td>
<td>22.1</td>
</tr>
<tr>
<td>182</td>
<td>22.5</td>
</tr>
<tr>
<td>198</td>
<td>22.9</td>
</tr>
<tr>
<td>213</td>
<td>23.3</td>
</tr>
<tr>
<td>228</td>
<td>23.6</td>
</tr>
<tr>
<td>244</td>
<td>24.0</td>
</tr>
<tr>
<td>259</td>
<td>24.3</td>
</tr>
<tr>
<td>274</td>
<td>24.7</td>
</tr>
<tr>
<td>277</td>
<td>24.7</td>
</tr>
<tr>
<td>277</td>
<td>24.7</td>
</tr>
<tr>
<td>277</td>
<td>24.7</td>
</tr>
<tr>
<td>278</td>
<td>24.7</td>
</tr>
<tr>
<td>282</td>
<td>24.8</td>
</tr>
<tr>
<td>297</td>
<td>25.2</td>
</tr>
<tr>
<td>313</td>
<td>25.5</td>
</tr>
<tr>
<td>328</td>
<td>25.8</td>
</tr>
<tr>
<td>343</td>
<td>26.1</td>
</tr>
<tr>
<td>358</td>
<td>26.4</td>
</tr>
</tbody>
</table>
2.4.3 Simulation Results

Before the CSMHyK module was added, the steady state conditions before hydrate formation were simulated in OLGA. The predicted temperature profiles and liquid holdup are shown in Figure 2.13 (left and right, respectively). The fluid temperature is shown to decrease along the length of the service line; the fluid cooled below the hydrate equilibrium line approximately 11 km from the wellhead. Liquid holdup is shown to gradually increase along the length of the service line as the heavier components in the gas phase condensed. The changes in elevation created little change in the condensate or water holdup.

The first hydrate plugging experiment to be simulated was Experiment 4 which was the restart of a depressurized line. In the experiment it was estimated from pressure changes that the plug had formed 6.5 km from the wellhead after 4 hours. In the simulation the plug formed 2 km from the wellhead after 5.5 hours (Figure 2.14 - left). The nucleation criterion was satisfied downstream of the wellhead less than one minute into the simulation due to the rapid pressure increase, and corresponding increase in the hydrate equilibrium temperature, on restart. The plug slowly moved
downstream as the warm reservoir fluids dissociated the hydrate on the upstream of the blockage, and the dissociated water reformed hydrate on the downstream side of the blockage. The discrepancy in the location of the hydrate plug is attributed to the slip factor being set to zero in the simulation; hydrates accumulated where they formed. If a higher slip factor was used in the simulations then the hydrates flowed out of the line with the condensate without such a large spike in the viscosity ratio (Figure 2.14 - right). In reality, the hydrate aggregates might have been transported further down the pipeline until they jammed in a restriction or dip section.

Mass transfer and internal heat transfer resistances are not accounted for in CSMHyK version 1.0, therefore the rate of hydrate formation in the simulations is either limited by the rate of heat removal from the pipeline, by the availability of water, or by intrinsic kinetics. Since the fraction of water in the Tommeliten line was less than 1 vol%, hydrate formation in these simulations was limited by the availability of water. The water was rapidly depleted upon hydrate nucleation from 2 km from the wellhead onwards (Figure 2.15). In addition, the diameter of the service line was only 6 inches so the surface to volume ratio for heat removal from the line was high; for larger diameter lines the formation rate could be limited by heat removal from the pipeline as the fluids warm up to the hydrate equilibrium temperature from the exothermic heat of hydrate formation.

In the next experiment, Experiment 5, a hydrate plug was allowed to form during steady state operation following an induced failure of methanol injection at the wellhead. The methanol concentration measured on the platform was less than 1 wt% when hydrates started to form (Austvik et al. 1995) so the hydrate formation curve for no hydrate inhibitor was used for the simulations. In the experiment, a hydrate plug formed after 6 hours in the same location as observed in the previous
Figure 2.14. A Profile Plot for the Service Line at 5.5 Hours with a slip factor of 0 (left) and a Profile Plot for the Service Line at 5.5 Hours with a Slip Factor of 0.1 (right) for Experiment 4

Figure 2.15. Temperature and Liquid Holdup Profile of the Service Line at 5.5 Hours with a Slip Factor of 0 for Experiment 4
experiment: 6.5 km from the wellhead. In the simulation, a hydrate plug formed at the base of the riser after only 1.3 hours (See Figure 2.16 - left). The base of the riser provided the right combination of subcooling and accumulated water to form a plug. The short timescale for this plug to form is an artifact of the zero slip condition. In reality some hydrate would be transported out of the pipeline as aggregates prior to plugging. The early formation of the hydrate plug in the riser could also be the result of using the hydrate formation curve with no hydrate inhibitor. The simulation neglects the time that the under-inhibited water displaces the initially inhibited water in the pipeline. Further into the simulation, the plug in the riser restricted the flow rate of the production fluids through the pipeline allowing the fluids to cool below the hydrate equilibrium line further upstream. Liquids also began to accumulate in the pipeline, and a second hydrate plug formed 5 km from the wellhead after 6.3 hours (Figure 2.16 - right), further restricting the flow.

In Experiment 6, the pipeline was restarted after a 16 hour pressurized shut-in. The shut-in pressure was approximately 120 bar. Upon restart, the system continued
Figure 2.17. A Profile Plot for the Riser at 0.5 Hours (left) and a Profile Plot for the Service Line at 5 Hours (right) for Experiment 6

to flow for 40 hours, during which time pressure fluctuations and gamma ray densitometer readings indicated that hydrate aggregates were flowing out of the line. After 40 hours the system plugged in the same location as in the earlier experiments: 6.5 km from the wellhead. In the simulation, hydrate plugs formed both in the base of the riser after 0.5 hours and 5 km from the wellhead after 5 hours (Figure 2.17). The viscosity spikes formed and dissipated as the hydrate accumulations were diluted by condensate slugs. The discrepancy in the location of the plug is again attributed to the zero slip condition applied to the simulations.

In Experiment 8, the pipeline was restarted following a 23 hour shut-in where the pipeline was left pressurized at 130 bar with a low concentration of methanol. The methanol concentration was too low to thermodynamically inhibit hydrates. When the line was restarted, no additional methanol was added. The hydrate formation curve without methanol was used in the simulation, since CSMHyK version 1.0 only allows a single hydrate formation curve to be used. In the experiment, a hydrate plug formed close to the platform after 13 hours. In the simulation, plugs formed and dissipated further upstream from 3 hours onwards (Figure 2.18); after 13 hours
the hydrates had accumulated into a substantial flow restriction approximately 5 km from the wellhead. The location of the plug was not reported in this experiment.

Although \textit{CSMHyK version 1.0} predicted the correct range of timescales for hydrate plug formation, the physical basis for gas-dominated systems, with particular regard to the transportation and jamming of hydrate aggregates may be overly simplistic. In order to simulate a hydrate plug in \textit{CSMHyK—OLGA}, the slip factor had to be reduced to zero, in effect forcing the hydrates to stay in the same location as they first formed. In reality, hydrate aggregates would be transported further down the pipeline before jamming. No mass or internal heat transfer limitations are incorporated into this version of \textit{CSMHyK}, so the rate of hydrate formation in the simulations was limited by the availability of water. This represents a maximum or worst case prediction for the amount of hydrate formed. This example demonstrates that \textit{CSMHyK—OLGA} can be a convenient tool to estimate the order of magnitude of the timescale for hydrate plug formation in a subsea tieback. In order to make the predictions more accurate and to capture the correct location for hydrate plug formation, a growth model for gas dominated systems, incorporating mass and internal heat transfer resistances is needed, together with a model for hydrate deposition, sloughing and jamming.
Figure 2.18. A Profile Plot for the Service Line at 3 Hours for Experiment 8
2.5 Conclusions

The key findings from Chapter 2 are as follows:

1. The predicted hydrate formation rate in the kinetic model is too fast since mass and heat transfer resistances are not considered. However, the lumped parameter from the flowloop simulations may not transfer to the field.

2. The kinetic model can be a useful tool to give a worst-case prediction of the hydrate formation rate for simulations where the formation rate is limited by water availability or heat removal from the system.

3. For the Tommeliten field trials, the predicted timescale for hydrate plug formation was correct but the predicted location was too far upstream.
Chapter 3

INTEGRATING THE TRANSPORT RESISTANCES TO HYDRATE FORMATION

The growth rate of hydrate in the kinetic model (Chapter 2) was calculated from a chemical kinetics equation (Equation 2.1) using temperature as the driving force for hydrate formation. An adjustable parameter that had been regressed to industrial flowloop data was used to account for the mass and heat transfer resistances in the flowloop. One problem with this approach was the reliability of the scale-up of the model to flow lines. In order to address this problem, a study was initiated into the mass and heat transfer resistances to hydrate formation in oil dominated systems. In this chapter, a revised hydrate formation model is presented based on mass and heat transfer between a growing hydrate particle and the bulk oil phase. The physical basis of the model is described in Section 3.1 and a sensitivity analysis on the model is presented in Section 3.2. The integration of the transport model into OLGA version 5.3.2.1 is described in Section 3.3. The transport model is adapted to simulate a stabilized flow concept in Section 3.4. Finally, the conclusions of this chapter are presented in Section 3.5.

3.1 The Physical Basis of the Transport Model for Hydrate Formation

A conceptual picture for hydrate formation in water-in-oil (W/O) emulsions was presented by Turner (2005) and is displayed in Figure 3.1. There are two critical interrelated steps in the formation of a plug: hydrate growth and hydrate agglomeration;
hydrate growth is the focus of this work.

First, water droplets are entrained into the oil phase; the size distribution of these entrained droplets has been studied extensively by Boxall (2009). Next, the entrained water droplets experience a hydrate nucleation event; hydrate nucleation is a stochastic process, but a rule-of-thumb of 6.5°F (3.6°C) was suggested by Matthews et al. (2000). Upon hydrate nucleation, a hydrate film rapidly forms around the water droplets; hydrate film growth processes have been studied by a number of researchers (See Chapter 5). At longer timescales, the hydrate formation rate becomes increasingly limited by the mass transfer of the hydrate formers across the hydrate film (See Chapter 6). Once formed, it is assumed that the hydrate particles remain dispersed in the oil phase. In addition, the hydrate films are assumed to remain intact as the shell thickens and particles collide. All droplets are assumed to nucleate simultaneously so droplet-particle collisions are not considered. A detailed conceptual picture of the droplets converting to hydrate particles was presented by Taylor (2006) and is shown in Figure 3.2.

The hydrate formation model proposed here considers three factors: mass transfer limitations, heat transfer limitations and intrinsic growth kinetics. In order to simplify the calculation procedure, a quasi-steady state was assumed which neglects the effects of changes in temperature and concentrations. This assumption is valid for
systems close to steady state where changes in concentration and temperature within the system are slow compared to the transport rates across the shell.

The hypothetical hydrate formation rate from a purely mass transfer limited process was calculated and compared to that for a purely heat transfer limited process and to a kinetically limited process. For heat transfer limited hydrate formation, the growing surface of the hydrate would be at the hydrate equilibrium temperature; for a mass transfer limited process, the growing surface of the hydrate would be at the equilibrium concentration of the guest or host molecule. In order to account for the resistances of sequential mass and heat transfer processes, the resistances were summed. The hydrate formation rate was determined by the slowest step: mass transfer, heat transfer or intrinsic kinetics. A conceptual picture of the mass and heat transfer limitations for a growing hydrate particle is shown in Figure 3.3.

3.1.1 External Transport Resistances in the Inertial Subrange

The mass transfer to a sphere in turbulent flow is defined by the empirical expression originally proposed by Frösslings (1938) and shown in Equation 3.1. The diffusivity of the hydrate former - methane - can be found from the Wilke and Chang (1955) correlation (Equation 3.2), where $D_{AB}$ represents the diffusivity of species A in species B, $\phi_B$ is the association factor of B, $M_B$ is the molecular weight of B, T is
the temperature, $\mu$ is the viscosity of B and $V_A$ is the molar volume of A. Frössling’s original equation was developed from boundary layer theory and validated using experiments on evaporating droplets 100 to 900 $\mu$m in diameter. However, the equation has since proven useful in many broader industrial applications provided that the droplets are in the inertial subrange (Middleman 1965), which is the case for low viscosity fluids. Another important limitation with the Frössling equation is that it does not consider the effect of surface active components on the mass transfer rate. Surface active components can provide an additional barrier to mass transfer and a reduction of 30-70 \% on the rates predicted by Frössling’s equation (Rosso et al. 2006).

One key unknown in applying the Frössling Equation to industrial scale systems is the velocity of the continuous phase relative to the droplet. Since most pipelines will be operated in the turbulent flow regime, the droplet velocity relative to the surrounding fluid is assumed to be equal to the root-mean-square of the fluctuating component of the velocity. This assumption will be valid inside the inertial subrange. The root-mean-square of the fluctuating component of the velocity can be derived from classical fluid mechanics. In a paper presented to the Royal Society, Reynolds
(1886), proposed that the turbulent shear stress between two adjacent layers of fluid, $\tau$, is given as the product of the fluid density $\rho$, and the fluctuating components of the velocity, $u'$ and $v'$, in the x and y direction respectively (See Equation 3.3).

$$Sh = 2 + 0.6Re^\frac{1}{3}Sc^3$$

(3.1)

$$D_{AB} = \frac{1.86 \times 10^{-18} \sqrt{\varphi_B M_B T}}{\mu V_A^{0.8}}$$

(3.2)

$$\tau = \rho u'v'$$

(3.3)

Further, Prandtl (1925) suggested that the fluctuating components of the velocity in the x and y direction ($u'$ and $v'$) are of the same order of magnitude, and that close to the wall the turbulent stress, $\tau$, is approximately equal to the wall stress $\tau_w$. Given these two approximations, the root-mean-square of the velocity fluctuations may be expressed by Equation 3.4, this velocity is known as the frictional velocity $u_{frictional}$ which can in turn be calculated from the superficial fluid velocity $u_{superficial}$ and the Fanning friction factor $f$. These approximations should only be valid close to the wall, but outside of the viscous sublayer. However it has been shown experimentally (Laufer 1952) that the energy diffusion rate in turbulent flow is sufficient that Equation 3.4 is a good approximation for the whole pipe diameter. The ratio of the root-mean-square of the velocity fluctuations to the frictional velocity was found to only vary from 0.8 to 2.4 from the center of the pipe to the edge of the viscous sublayer for a wide range of Reynolds numbers (50,000 to 500,000) for a pipe diameter of 25.4 cm (10 inches) and fluid velocities of 3 to 30 m/s (10 to 100 ft/s). The original experimental data of Laufer (1952) are reproduced in Figure 3.4.
$$\sqrt{v'^2} \approx \sqrt{\frac{\tau_w}{\rho}} = v_{\text{frictional}} = u_{\text{superficial}} \sqrt{\frac{f}{2}}$$ \hspace{1cm} (3.4)$$

For laminar flow, the Fanning friction factor $f$ can be found from Equation 3.5; for turbulent flow, the Blasius (1913) equation (Equation 3.6) can be used.

$$f = \frac{16}{Re}$$ \hspace{1cm} (3.5)

$$f = 0.079Re^{-\frac{1}{4}}$$ \hspace{1cm} (3.6)

### 3.1.2 External Transport Resistances in the Viscous Subrange

For high viscosity fluids the hydrate particles may be inside the viscous subrange, where the hydrate particles are smaller than the eddies in the fluid. In this subrange, Friedlander (1957, 1961) and Middleman (1965) suggested alternative correlations for the Sherwood number based on the Peclet Number. These correlations are shown in Equations 3.7 (Middleman 1965) and 3.8 (Friedlander 1961) for low and high Peclet numbers respectively. For intermediate Peclet numbers ($1 < Pe < 100$) the Sherwood number increases almost linearly (Friedlander 1961), a linear interpolation was therefore used as shown in Figure 3.5.

$$Sh = 2 \left(1 + 0.25Pe_{\text{mass}} + 0.083Pe_{\text{mass}}^2 + \ldots\right) \text{ ; } Pe_{\text{mass}} < 1$$ \hspace{1cm} (3.7)

$$Sh = 0.991Pe_{\text{mass}}^{\frac{1}{3}} \text{ ; } Pe_{\text{mass}} > 100$$ \hspace{1cm} (3.8)

In the viscous subrange, the velocity of the particles relative to the surrounding fluid will be lower than the velocity of the eddies since the particles will entrained by
Figure 3.4. The Experimental Data of Laufer (1952) Showing the Variation of the ratio of the Fluctuating Component of the Velocity to the Frictional Velocity against the Radial Position
Figure 3.5. A Plot Showing the Effect of Peclet Number on the Predicted Sherwood Number Using the Correlations Presented in Equations 3.7 and 3.8 with a Linear Interpolation for the Transition Range
the eddies. The velocity of the particles $v_{id}$, is approximately equal to the product of the length scale of the eddies $l_d$ and the local shear rate $\dot{\gamma}_{ld}$ as shown in Equation 3.9.

$$v_{id} \approx l_d \dot{\gamma}_{ld} \quad (3.9)$$

From the Taylor (1934) criterion for laminar shear flow, the value of the Capillary number is unity (Equation 3.10). This can be used to provide an expression for the local shear rate $\dot{\gamma}_{ld}$ in terms of the interfacial tension $\Gamma$, the droplet diameter $d_{drop}$, and the continuous phase viscosity $\mu$ as shown in Equation 3.11. Substituting Equation 3.11 into Equation 3.9 gives Equation 3.12.

$$\frac{\mu \dot{\gamma}_{ld} d_{drop}}{\Gamma} = 1 \quad (3.10)$$

$$\dot{\gamma}_{ld} = \frac{\Gamma}{\mu d_{drop}} \quad (3.11)$$

$$v_{id} = \frac{\Gamma l_d}{\mu d_{drop}} \quad (3.12)$$

Kolmogorov (1941) demonstrated how the length scale of the turbulence $l_d$ can be related to the fluid kinematic viscosity $\nu$ and the energy dissipation rate per unit volume $\varepsilon$. This dependence is shown in Equation 3.13.

$$l_d = \left[ \frac{\nu^3}{\varepsilon} \right]^{\frac{1}{4}} \quad (3.13)$$

From an energy balance on fluid flow in a pipe, the rate of mechanical energy loss in a pipe is equal to the product of the pressure drop in the system and the volumetric flow rate (See Equation 3.14). Substituting the Darcy-Weisbach equation
(Equation 3.15 for the pressure drop gives an expression for the energy dissipation rate per unit volume (Equation 3.16).

\[ \varepsilon = \frac{\Delta PQ}{\pi D^2 L} \quad (3.14) \]

\[ \Delta P = \frac{2f \rho u^2 L}{D} \quad (3.15) \]

\[ \varepsilon = \frac{2f u^3}{D} \quad (3.16) \]

The heat transfer analogs to the above listed mass transfer correlations are shown in Equation 3.17 for the inertial subrange and Equations 3.18 and 3.19 for the viscous subrange.

\[ Nu = 2 + 0.6Re^{\frac{1}{3}}Pr^{\frac{1}{3}} \quad (3.17) \]

\[ Nu = 2 \left(1 + 0.25Pe_{\text{heat}} + 0.083Pe_{\text{heat}}^2 + \ldots\right) \quad ; \quad Pe_{\text{heat}} < 1 \quad (3.18) \]

\[ Nu = 0.991Pe_{\text{heat}}^{\frac{1}{3}} \quad ; \quad Pe_{\text{heat}} > 100 \quad (3.19) \]

### 3.1.3 Internal Transport Resistances

Several theoretical and empirical models have been proposed for heat transfer in porous media. The two extreme theoretical models are the parallel model and the series model. Both models assume that each of the phases comprising the composite material phases are layered. The parallel model assumes that heat is conducted
parallel to the layers. The series model assumes the heat is conducted perpendicular to the layers. The parallel model represents a maximum thermal conductivity and the series model represents a minimum. For heat conduction through a hydrate shell, it is assumed that the pores are perpendicular to the surface of the shell, and hence heat is conducted parallel to the layers. The parallel model is given in Equation 3.20 where $\epsilon$ represents the hydrate porosity, and $k$ represents the thermal conductivity of each phase. The pores are assumed to be filled with water. The heat transfer rate through the hydrate shell $Q$, was then found from Fourier’s Law (Equation 3.21).

$$k_{\text{composite}} = \epsilon k_{\text{water}} + (1 - \epsilon)k_{\text{hydrate}}$$ (3.20)

$$Q = -4\pi r^2 k \left| \frac{dT}{dx} \right|_{x=r_p}$$ (3.21)

There are a number of alternative models for mass transfer across a hydrate film; some assume water is predominantly transported through the shell through a capillary permeation mechanism (Topham et al. 1984; Mori and Mochizuki 1996; Sugaya and Mori 1996; Mori and Mochizuki 1997), others propose that the hydrate guest (Staykova et al. 2003; Kuhs et al. 2006; Demurov et al. 2002; Peters et al. 2008) or the host (Shindo et al. 1995) molecules diffuse through the hydrate shell through pores or faults.

The mechanism of mass transfer across a hydrate shell is discussed in detail in Chapter 5, but for the development of this model, two mechanisms are considered: the permeation of water through pores in the shell, and the diffusion of the hydrate formers through the hydrate shell. The faster of the two mechanisms will determine the hydrate formation rate.

In the diffusion-based model, the diffusing molecule is assumed to be predom-
inantly methane. The mass flux of methane through the hydrate shell \( J_{\text{gas}} \), was calculated from steady state Fickian diffusion using Fick’s First Law - Equation 3.22.

\[
J_{\text{gas}} = -D_A \left. \frac{dC}{dx} \right|_{x=r_p}
\]  

(3.22)

The water permeation rate through a porous hydrate shell was given by Mori and Mochizuki (1996) and is shown in Equation 3.23. The water permeation rate was derived from the Hagen-Poiseuille equation. \( J_{\text{water}} \) represents the mass flux of water through the shell, \( \Gamma \) is the interfacial tension, \( \rho \) is the water density, \( \epsilon \) is the porosity, \( r_{\text{pore}} \) is the pore diameter, \( \theta \) is the contact angle of water on hydrate, \( \mu \) is the water viscosity, \( \delta \) is the hydrate shell thickness and \( \tau \) is the pore tortuosity.

\[
J_{\text{water}} = \frac{\Gamma \rho \epsilon r_{\text{pore}} \cos \theta}{4\mu \delta \tau^2}
\]  

(3.23)

The concentration and thermal gradients at the particle surface for the quasi-steady state internal mass and heat transfer are given by Equations B.11 and B.12 respectively. The internal and external transport resistances are then summed as shown in Equations 3.24 and 3.25, where \( r_p \) and \( r_c \) are the diameters of the hydrate particle and water core, \( \Delta C \) and \( \Delta T \) are the concentration and temperature driving forces, and \( k \) and \( h \) are the mass transfer coefficient and convective heat transfer coefficient found from the Sherwood and Nusselt numbers respectively.

\[
\frac{dm}{dt} = \frac{4\pi r_p^2 \Delta C}{\frac{1}{k} + \frac{r_p-r_c}{D_A} \frac{r_c}{r_c}}
\]  

(3.24)

\[
Q = \frac{4\pi r_p^2 \Delta T}{\frac{1}{h} + \frac{r_p-r_c}{k_{\text{composite}}} \frac{r_p}{r_c}}
\]  

(3.25)
Table 3.1. The Base Case Values for the Sensitivity Analysis

<table>
<thead>
<tr>
<th>Input Parameters</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>4</td>
<td>°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>43.1424</td>
<td>bar</td>
</tr>
<tr>
<td>Diameter of the Pipe</td>
<td>0.1016</td>
<td>m</td>
</tr>
<tr>
<td>Superficial Velocity of the Water Phase</td>
<td>3</td>
<td>m/s</td>
</tr>
<tr>
<td>Superficial Velocity of the Oil Phase</td>
<td>3</td>
<td>m/s</td>
</tr>
<tr>
<td>Water Holdup</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>Oil Holdup</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>Droplet Diameter</td>
<td>40</td>
<td>µm</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Hydrate Porosity</td>
<td>$5 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>Pore Diameter</td>
<td>5</td>
<td>nm</td>
</tr>
<tr>
<td>Contact Angle</td>
<td>5</td>
<td>°</td>
</tr>
<tr>
<td>Interfacial Tension</td>
<td>25</td>
<td>mN/m</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>$5 \times 10^{-15}$</td>
<td>m²/s</td>
</tr>
<tr>
<td>Shell Thickness</td>
<td>10</td>
<td>µm</td>
</tr>
</tbody>
</table>

3.2 A Sensitivity Analysis on the Transport Model

In order to identify the critical unknown parameters in the hydrate growth model, a sensitivity analysis was performed on the first-pass transport model.

The base case values selected for the analysis are shown in Table 3.1, and the results are shown in Figure 3.6. The rate of hydrate growth was calculated for the base case values. Then, each parameter was adjusted in turn, and the new growth rate was calculated. The most sensitive parameters are shown to be the diameter of the water droplets, followed by the diffusivity of methane through the hydrate shell. The pore diameter, porosity and tortuosity had no effect on the growth rate predictions for the range investigated since molecular diffusion of the hydrate formers was the predominant internal mass transfer mechanism.
Figure 3.6. A Sensitivity Analysis on the Key Parameters in the Transport Model
3.3 The Integration of the Transport Model into OLGA

In order to integrate the transport model with OLGA, a number of additional input parameters were needed. Some of these parameters were available from OLGA, others required lookup tables to be generated.

3.3.1 Inputs and Outputs

Some of the additional system parameters such as the pipe diameter were already entered by the user into OLGA and could be passed on to CSMHyK. Other system parameters were available as outputs from the simulator; these properties included the superficial velocities of the aqueous and oil phases and the volumetric holdup of the aqueous and oil phases. Many of the fluid properties that were required by the transport model were already available from the fluid property table which must be generated before running an OLGA simulation. The properties of the aqueous and oil phases that were passed to the transport model from the fluid property table included: the thermal conductivities, the specific heat capacities, the densities, and the viscosities. The diffusivity of methane through the hydrate shell was added as an additional user input in OLGA, a default value of $1 \times 10^{-16} \text{m}^2/\text{s}$ was included based on the literature which is between $1 \times 10^{-17}$ and $1 \times 10^{-16} \text{m}^2/\text{s}$ (Kuhs et al. 2006).

Supplemental output parameters were also added to CSMHyK to provide the user with additional information on the state of the simulation. One such output parameter was the limiting mechanism which is an integer with a value from 1 to 8 that indicates the rate-limiting step in the hydrate formation process:

1 = Intrinsic kinetics
2 = External mass transfer
3 = External heat transfer
4 = Internal heat transfer
5 = Internal mass transfer
8 = Hydrate has not nucleated yet

Output parameters from the mean droplet size correlations developed by Boxall (2009) were also included in the transport model, namely: the subrange for the droplet calculations (1 = Inertial, 2 = Viscous), the calculated mean droplet diameter (m), the droplet diameter calculated from the inertial subrange (m), the droplet diameter calculated from the viscous subrange (m), the Weber number, the critical Weber number, and the Reynolds number.

Finally, the interparticle adhesion force was included as an output; the adhesion force in the transport model is calculated from the subcooling based on experimental data for dry cyclopentane hydrate particles (Dieker, 2009). A complete list of the additional input and output parameters for the transport model is provided in Table A.2.

### 3.3.2 Lookup Tables

Some of the parameters required for the transport model were not available from OLGA so additional tables are needed to capture the pressure and temperature dependence of these parameters. Look-up tables were needed for: the concentration of methane in the oil phase, the concentration of methane in the water inside of the hydrate shells, and the molecular weight of the oil phase. The tables must be generated prior to a simulation by performing a series of flash calculations for the full range of pressure and temperature conditions of interest. Three methods were developed to generate the look-up tables: spreadsheets linked to PVTsim or Multiflash, and a modified version of CSMGem.
3.3.3 Tracer Tracking

One of the main limitations of the kinetics model for hydrate formation was that only a single hydrate equilibrium P-T curve could be used (Creek, 2006). This meant that systems containing salt or another thermodynamic inhibitor could not be accurately simulated unless the concentration of the inhibitor was constant. This problem was overcome in the transport model by linking the tracer tracking module in OLGA to the hydrate formation model - CSMHyK. The tracer tracking module simulates how a water or oil-borne marker would move through the OLGA simulation. A tracer is defined and the carrier phase is specified. Next a tracer source is added to the simulation and the mass flow of tracer as a function of time is defined. The concentration, age, and time subcooled for up to two tracers can then be sent to CSMHyK.

In the transport model, the concentration of the first tracer is used to adjust the hydrate equilibrium temperature, in effect shifting the P-T curve to higher pressures and lower temperatures as the concentration of the tracer increases. The hydrate equilibrium temperature is adjusted by using an additional look-up table, this time in P-X space, which is prepared in advance of the simulation. CSMHyK version 2.0 will interpolate between the inhibitor concentrations and pressures of interest to return a new hydrate equilibrium temperature. This approach provides a way to overcome the previous problem of only one P-T curve for hydrate equilibrium without a fully compositional model which would be incompatible in OLGA. A limitation of this approach is that it will not capture the phase behavior of the thermodynamic inhibitor as it approaches the solubility limit. Another problem is that in some cases a small amount of hydrate formation can cause a large shift in the salt concentration in the remaining water phase which in turn will cause a large
change in the hydrate equilibrium temperature. In some cases this rapid change to 
the hydrate equilibrium temperature will lead to numerical instabilities within the 
\textit{OLGA} simulation which manifest themselves as oscillations in the hydrate formation 
rate and fluid temperature.

\textit{CSMHyK} version 2.0 with \textit{tracer tracking} may be of use for systems where 
a thermodynamic inhibitor is injected part way through the system, where an uninhibited line is mixed with an inhibited line, or when hydrate formation itself causes 
an increase in the inhibitor concentration of the remaining water phase. A further 
application - particle tracking - is discussed more in Section 3.4.2.

3.4 Adaptation of the Transport Model for Stabilized Flow

In the \textit{CONWHYP} stabilized flow process (Larsen et al. 2001), a fully converted 
hydrate slurry is pumped around a subsea recycle loop. In one part of the loop, a 
small amount of unconverted water is added from a wellstream. The unconverted 
water contacts the fully converted hydrate slurry, the water coats the dry hydrate 
particles and rapidly converts to dry hydrate. Part of the dry hydrate slurry can then 
be transported to the downstream processing facilities and the rest of the slurry is 
recycled back around the loop. This concept is illustrated in Figure 3.7. It is well 
known that wet hydrate particles are more prone to agglomeration than dry particles 
(Taylor et al. 2006) so it is vital to design a system so that the timescale for hydrate 
formation is much faster than the timescale for particle-particle collisions. A model 
for the formation rate of hydrate in such a stabilized flow system would be one of the 
requirements for designing a system in which dry hydrate particles could be formed 
without significant agglomeration. Prior to this work, no model for stabilized flow 
existed.
3.4.1 Modifications to the Growth Model

There are several differences between the CONWHYP mechanism for stabilized flow and the conceptual picture for hydrate formation from dispersed water droplets on which the transport model is based. Firstly, in the transport model a hydrate shell surrounds the outside of the water droplet; in the case of the stabilized flow mechanism a water film surrounds the dry hydrate particle. In the transport model the hydrate shell thickens over time as more hydrate is formed and the water core shrinks; in the stabilized flow concept the hydrate core grows at the expense of the water film. In the transport model, methane must diffuse through the hydrate shell to form hydrate on the inside of the shell; in the stabilized flow concept, the methane must diffuse through the water film to reach the growing crystal surface. In the transport model, particles are allowed to agglomerate as defined by the steady state force balance; in stabilized flow, agglomeration should not occur but particles will grow each time the particles are wet.
A summary of the differences between the transport model for hydrate plug formation and the stabilized flow mechanism is shown in Figure 3.8. The diffusivity of methane in water at 4°C was previously measured to be $8.5 \times 10^{-10} \text{m}^2/\text{s}$ (Witherspoon and Bonoli, 1969).

### 3.4.2 Particle Tracking

Another modification that was made to OLGA in order to simulate the stabilized flow process is particle tracking. In the kinetic model and the transport model, the need to track the movement of particles was avoided by conserving the initial droplet size distribution as water droplets convert to hydrate particles. The number of particles in each pipe section was then calculated by $CSMH_yK$ from the particle size and the volume fraction of water and hydrate. In the stabilized flow version of $CSMH_yK$ this approach was inadequate because the particles grow each time they enter the mixing zone, and the particle size is changing accordingly. Therefore, it is necessary to track how many particles are in each pipeline section at a given time, and how they move and how they are removed from the pipeline. In addition it will be necessary to model particle breakup by the pump, otherwise particles will continue to grow after each pass through the mixing zone, eventually plugging the pipeline.
In the short term, a second *tracer tracking* model was used to track the particles. In the case of particle tracking, the carrier phase for the particle tracer was specified as the oil phase. The tracer concentration (kg/m$^3$ of pipe) was used as a direct analogy for the particle concentration (particles/m$^3$ of pipe). The number of particles in the pipeline section is sent from *OLGA* to *CSMHyK*. As yet, *CSMHyK* is unable to update the number of particles in the *OLGA* tracking model. Particles therefore need to be added separately to *OLGA* using a particle source. Additional particle sources can be added into the *OLGA* model to account for particle breakup by the pump. The *CSMHyK* stabilized flow model will constantly recalculate the particle size by dividing the volume of hydrate evenly between the number of particles provided by the tracer model.

This approach is somewhat cumbersome since the number of particles in the tracer model must be specified manually in the *OLGA* input file to coincide with the desired particle size for the volume of water and hydrate in the system.

### 3.5 Conclusions

The key conclusions for Chapter 3 are as follows:

1. A new model for hydrate formation has been proposed based on transport resistances.

2. A sensitivity analysis on the new model has shown that the surface area and the effective diffusivity of the hydrate formers through the hydrate shell are the most sensitive parameters.

3. The *tracer tracking* module in *OLGA* has been linked to *CSMHyK* to account for the effect of changing concentrations of thermodynamic inhibitor on the
hydrate equilibrium temperature.

4. The transport model has been modified to simulate the CONWHYP stabilized flow process.
Chapter 4

STUDIES OF HYDRATE NUCLEATION WITH DIFFERENTIAL SCANNING CALORIMETRY

One of the key unknowns in predicting the rate of hydrate formation in a flow line is the subcooling criterion for hydrate nucleation. In previous versions of CSMHyK, a subcooling criterion of 6.5°F (3.6°C) was applied (Boxall et al. 2008 b). However, this approach negates the time dependence of hydrate formation since it is possible to form hydrate if a system is exposed to lower subcoolings for longer time scales. In this chapter, high pressure Differential Scanning Calorimetry was applied to the problem of hydrate nucleation. Experiments with constant temperature or constant cooling rate were performed to study the hydrate nucleation tendency at low and high subcoolings.

The apparatus and experimental procedures are described in Sections 4.1 and 4.3. The results for the constant cooling rate experiments are presented in Section 4.4.1 and the results for the constant temperature experiments are presented in Section 4.4.2. The implications of these measurements are discussed in Section 4.5. Finally, the key conclusions from this chapter are presented in Section 4.6.

4.1 A Review of Previous Literature on Hydrate Nucleation.

Classical nucleation theory was developed from the 1920s (Volmer and Weber 1926; Becker and Döring 1935). The theory describes the activation barrier to nucleation as the sum of the increase in free energy due to the creation of a new interface
and the decrease from creating a more stable phase. The interfacial energy is proportional to the square of the crystal radius, and the free energy associated with the phase change is proportional to the cube of the crystal radius. This leads to a maximum in energy with respect to radius as the daughter phase emerges; once a nucleus of the daughter phase reaches this critical radius through a series of random fluctuations, further growth is energetically favorable. Nucleation is of great importance in a diversity of disciplines from atmospheric science to industrial crystallization. A comprehensive review of nucleation theory and application is provided by Kashchiev (2000).

Primary nucleation is divided into two broad categories: homogeneous and heterogeneous. Homogeneous nucleation occurs when a critical nucleus emerges directly from the parent phase. At low subcoolings this can have a very low probability since the critical radius can be appreciable. In the case of hydrate formation from air inclusions in ice cores, nucleation can take thousands of years (Ohno et al. 2004; Salamantin et al. 1998, 2001; Shimanda et al. 2004). At higher subcoolings, the difference in free energy between the parent and daughter phase increases, this shifts the critical nucleus to smaller radii. At sufficiently high subcooling, homogeneous nucleation becomes deterministic; this point is known as the spinodal.

In heterogeneous nucleation the cluster grows in contact with a third phase which lowers the interfacial energy cost of further growth, hence smaller clusters of the daughter phase are required for energetically favorable growth. The energy barrier associated with heterogeneous nucleation is therefore much smaller than for homogeneous nucleation, hence phase transitions can occur more rapidly in the presence of impurities.

In the case of dispersed systems such as emulsions, droplets can behave as inde-
Pendent reactors (Dalmazzone et al. 2006; Clusse D. et al. 2005; Lachance 2008) and the nucleation of one droplet may not necessitate the nucleation of adjacent droplets. However, droplet collisions in sheared systems or in concentrated emulsions may cause nucleation propagation between droplets; this is known as secondary nucleation.

Nucleation of a hydrate phase has been a source of interest and frustration in the hydrate community for a number of years. The stochastic nature of the nucleation event can often lead to large variations in the onset time between experiments (Maini and Bishnoi 1981; Englezos et al. 1987; Christiansen et al. 1994). Researchers have also focused on the molecular mechanisms for hydrate nucleation (Sloan and Fleyfel 1991; Radhakrishnan and Trout 2002; Walsh et al. 2009), but a major drawback has been the difficulty in obtaining sufficient laboratory data on a small enough time or length scale to validate the proposed mechanisms.

Perhaps the most important step towards a systematic laboratory study of the hydrate nucleation phenomenon has been the construction of the Automated Lag Time Apparatus or ALTA (Barlow and Haymet 1995; Heneghan et al. 2001). The ALTA enables multiple repetitions of nucleation experiments under identical conditions, and can generate large quantities of statistical data on the nucleation tendency of a system.

ALTA studies of heterogeneous hydrate nucleation from a model water-soluble hydrate former, tetrahydrofuran, THF, (Wilson et al. 2005; Wilson and Haymet, 2008), have shown that with constant cooling, a narrow temperature range of a few degrees can cause an increase in the probability of nucleation from almost zero to close to 100%. Before this temperature is reached, it is this very low probability of nucleation that leads to the large variations in nucleation times. While this has been shown for THF hydrate, it is not clear whether this narrow temperature range exists
for gas phase hydrate formers, which are more hydrophobic and hence have a very low solubility in water. In subsequent work (Dalmazzone D et al. 2006), isothermal methane hydrate nucleation in water-in-oil emulsions was studied by high pressure Differential Scanning Calorimetry. It was shown that the hydrate nucleation peak becomes narrower and more symmetrical at higher subcoolings, indicating a shorter nucleation time.

In this study, Differential Scanning Calorimetry was applied to determine the hydrate nucleation point for gas phase hydrate formers. Constant cooling ramps were performed to study the effects of cooling rate and subcooling on the nucleation point at high subcoolings. Complementary isothermal measurements were performed to better understand the factors that affect the time required for hydrate nucleation under lower subcoolings.

4.2 A Description of the High Pressure Differential Scanning Calorimeter

Differential Scanning Calorimetry (DSC) is a widely used technique to study the thermal properties of a sample (Sorai, 1998). A Differential Scanning Calorimeter consists of a sample cell and a reference cell. During an experiment, both cells are heated or cooled according to a pre-programmed temperature profile. The difference in heat flux required to obtain a zero temperature difference between the sample and reference cells can be analyzed to determine the thermal properties of the sample, such as specific heat capacity, or the latent heat associated with phase changes.

The High Pressure DSC used for this work was a HP-micro DSC VII from Setaram Instruments. A schematic of the DSC and the associated high pressure panel is shown in Figure 4.1. The high pressure cells were made of corrosion resistant Hastelloy C276 with an internal diameter of 0.64 cm and a height of 1.95 cm. The cells
Figure 4.1. A Schematic of the High Pressure DSC Apparatus with High Pressure Panel (rated to 400 bar) and Data Acquisition System (Setaram, 2003)

were contained within a furnace, the temperature of which was controlled by Peltier elements as shown in Figure 4.2. The DSC is calibrated to an accuracy of within 0.3°C (Setaram 2003).

4.3 Experimental Procedure for the Nucleation Measurements

Ultra high purity methane (99.99% purity, Airgas Inc.), xenon (Spectra Gases, UHP Grade) and HPLC grade water (Aldrich Inc.) were used in these experiments. For all of the experiments, the DSC cell was loaded with a known mass of water. The cell was then sealed, placed in the DSC and pressurized with the hydrate forming gas. Pressures ranging from 30 to 150 bar were investigated. A saturation period of 3 hours at 30°C was used to ensure that the water was fully saturated with the guest molecule before the temperature of the system was reduced into the hydrate formation
region. The saturation time was estimated using a 1D Fickian diffusion model. Two hydrate formation procedures were employed in this study: constant temperature and constant cooling. The temperature ramping experiments were performed with 40 mg of water and the isothermal experiments were performed with 175 mg of water. In the constant temperature experiments, the sample was cooled to an isotherm (-5°C, -7°C or -10°C) and held for a predetermined length of time to allow hydrate to nucleate. The nucleation of hydrate was indicated by an exotherm.

Following a pre-determined hold period, the sample was then heated to dissociate the hydrate, as indicated by an endotherm. For the constant cooling experiments, the temperature of the sample was reduced to -40°C at a constant cooling rate. In this case, hydrate nucleation occurred during the cooling period. Once the sample reached -40°C, it was then heated to dissociate the hydrate. Once the hydrate had dissociated, the sample was then held at 40°C for 1 hour to eliminate any residual hydrate structure (Wilson et al. 2008; Buchanan et al. 2005) before the experiment.
was repeated. Since nucleation is a stochastic process, the experiments were each repeated a number of times in order to capture the distribution in time or temperature.

A typical thermogram from a constant cooling rate experiment is shown in Figure 4.3. The experiment depicted was performed at a pressure of 200 bar and a cooling rate of 0.5°C/min. The nucleation of ice and hydrate is indicated by a spike in the heat flow from the sample cell. Although hydrate has a higher latent heat than ice, 460 J/g for sI hydrate (Handa, 1986) compared to 334 J/g for ice Ih, the magnitude of the ice peak was always greater than the hydrate peak since hydrate only forms at the gas-water interface whereas ice can form throughout the water phase. The phases can also be distinguished by the temperature at which the endotherm of melting occurs during the heating cycle.

A typical thermogram from a constant temperature experiment is shown in Figure 4.4. Hydrate nucleation occurred some time after the sample had been cooled to the isothermal temperature. Hydrate nucleation was again indicated by a small exotherm. No ice nucleation occurred in the experiment shown in Figure 4.4; ice nucleation leads to a much larger exotherm and an endotherm on heating at 0°C.

4.4 Results from the Nucleation Experiments

In all of the experiments, it was observed that hydrate nucleation occurred below 0°C. Therefore, ice formation was also possible but could be distinguished from hydrate formation as discussed in Section 4.3.

4.4.1 Constant Cooling Rate Experiments

A methane/water system and a xenon/water system were cooled using temperature ramping to determine the effect of the subcooling and cooling rate on the
Figure 4.3. An Example Thermogram from a Ramped Nucleation Experiment
Figure 4.4. An Example Thermogram from an Isothermal Nucleation Experiment
hydrate nucleation tendency: the temperature at which it occurred and its repeatability. Temperature ramping experiments were performed at 32, 100, 150, and 200 bar with cooling rates of 0.5, 1.5, and 3.0°C/min. In the temperature ramping experiments, the nucleation temperature was defined as the temperature at which the heat flux initially increased from the baseline. An example set of thermograms at 200 bar and 0.5°C/min is shown in Figure 4.5. Run 6 in Figure 4.5 also includes an ice nucleation exotherm at approximately -14°C.

For each hydrate former and for each pressure, the hydrate nucleated within approximately a 2°C temperature range. The average nucleation temperatures of ice and hydrate for the methane/water system are shown in Figure 4.6 for the four
Figure 4.6. A Pressure - Temperature Plot Showing the Temperature Range for Ice and Hydrate Nucleation for Ramped Experiments with Methane at Various Pressures. The Number of Experiments for Each Point is Displayed on the Plot.

Pressures investigated. The numbers on the plot represent the number of repeat experiments at that pressure and the error bars show the temperature range in which nucleation occurred for all of the experiments. A pressure increase from 32 to 200 bar changed the equilibrium temperature of the methane/water system from 2.1°C to 18.6°C.

In the 32 bar ($T_{eq} = 2.1°C$) and 100 bar ($T_{eq} = 5.1°C$) experiments, ice always formed before the hydrate and the onset point of hydrate nucleation was not statistically different between the 32 bar and 100 bar experiments at $-19±0.85°C$ and $-20±0.67°C$ respectively, even though the equilibrium temperature was $10°C$ higher.
for the 100 bar experiments. However, it should be noted that the presence of ice may have encouraged hydrate nucleation via associated hydrogen bonding. At 150 bar ($T_{eq} = 16.3^\circ C$), ice or hydrate formed first depending on the individual experiment. From the dissociation endotherms it appeared that in some cases hydrate had nucleated at the same time as ice but the hydrate nucleation peak was obscured by the ice exotherm. In one experiment, hydrate nucleation clearly occurred before ice nucleation at around $-12^\circ C$ or a driving force of $28^\circ C$. At 200 bar ($T_{eq} = 18.6^\circ C$), hydrate always formed before ice at $-12.9 \pm 0.45^\circ C$. Interestingly, the change in driving force between 150 and 200 bar roughly coincided with the change in hydrate nucleation temperature. It should be noted that ice formation always occurred in a range from $-14^\circ C$ to $-16^\circ C$ regardless of the system pressure or the presence of hydrate. The ice nucleation results for the methane/water system are shown in detail in Figure 4.7.

Although the effect of ice on the nucleation tendency of hydrate is not fully understood, these results suggest that when ice is not present, the hydrate nucleation temperature increases as the pressure of the system increases. However, when ice nucleated before hydrate, large changes in subcooling had little effect on the hydrate nucleation temperature.

To further investigate the effect of subcooling on hydrate nucleation, a xenon/water system was measured. Xenon is similar in size to methane but it is a much more stable hydrate guest which allowed high driving forces for hydrate formation to be attained without such large driving forces for ice nucleation. The xenon experiments were performed in the same manner as the methane/water system at pressures of 19.5 bar ($T_{eq} = 25.1^\circ C$) and 31 bar ($T_{eq} = 29.4^\circ C$). Figure 4.8 shows the fraction of samples that nucleated before a given temperature for these two pressures. At 19.5 bar, hydrate nucleated at $-5\pm0.7^\circ C$ which corresponded to a driving force of $30^\circ C$ which was very
Figure 4.7. Fraction of Samples in which Ice Nucleated During Ramped Experiments for Methane at Various Pressures and Ramping Rates
similar to the methane/water system. Hydrate nucleation occurred at -2.6±0.5°C for the 31 bar experiments. These temperature ramping experiments show that similar driving forces are needed to induce nucleation, without the presence of ice, for two different hydrate guests.

For both systems (methane/water and xenon/water), various cooling rates were employed (0.5, 1.5, and 3°C/min) to determine the effect on the hydrate nucleation temperature. The fraction of samples that nucleated for various cooling rates in methane/water systems in which ice formed first (32 bar and 100 bar) are shown in Figures 4.9 and 4.10, respectively. Figure 4.11 shows the fraction that nucleated in the case where hydrate formed first (200 bar). In both systems, a 2.5°C/min change
in cooling rate did not have a significant effect on the temperature range in which nucleation occurred. Figure 4.8 shows two cooling rates for the xenon/water system at 31 bar. As with the methane/water system, the nucleation point did not change significantly as the cooling rate was increased from 0.5 to 1.5°C/min.

It should be noted that although the absolute driving force needed for hydrate nucleation in these measurements was consistently around 30°C in the absence of ice, the absolute driving force required for hydrate nucleation is expected to be very dependent on the specifics of the system, i.e., volume, cell material and shear rate.
Figure 4.10. Fraction of Samples in which Hydrate Nucleated During Ramped Experiments for Methane at 100 bar
Figure 4.11. Fraction of Samples in which Hydrate Nucleated During Ramped Experiments for Methane at 200 bar
4.4.2 Constant Temperature Experiments

The temperature ramping experiments demonstrated that hydrate nucleation is essentially deterministic, within a narrow range of subcooling temperatures for a given system at a given pressure. The isothermal experiments with methane and pure water were performed at more moderate subcoolings in which hydrate nucleation could take several hours to occur. The results from these experiments further demonstrated that the time distribution for hydrate nucleation becomes narrower as the subcooling is increased.

Figure 4.12 shows hydrate nucleation results at 150 bar with 25°C subcooling (-10°C isotherm), 22°C subcooling (-7°C isotherm) and 20°C subcooling (-5°C isotherm). Increased subcooling led to a decrease in average nucleation time in these isothermal experiments. At 25°C subcooling (-10°C isotherm), hydrate nucleation occurred in the narrowest time range, from 0-200 minutes with most of the runs nucleating within 30 minutes. At a subcooling of 20°C (-5°C isotherm) the hydrate nucleation occurred over a wider time range, from 0-1200 minutes.

No significant effect of the gas composition on the time range for nucleation at a given isothermal temperature was observed (See Figure 4.13). Experiments were performed at -10°C with a structure II forming methane-ethane gas mixture and compared to similar results for methane gas which forms structure I. The subcooling at this temperature for the methane-ethane gas mixture was much greater than for the pure methane system (31°C compared to 26°C according to CSMGem), but no statistically significant difference in the time range for nucleation was observed. However, since only four experiments were performed with the methane-ethane mixture it is difficult to draw a definitive conclusion from these results alone and more measurements are needed.
Figure 4.12. Fraction of Samples in which Hydrate Nucleated During Isothermal Experiments for Methane at 150 bar
Figure 4.13. Fraction of Samples in which Hydrate Nucleated During Isothermal Experiments for Pure Methane and for a 75 mol% Methane - 25 mol% Ethane Mixture at 150 bar
4.5 Implications of the Nucleation Experiments

The nucleation trends observed in this work are in good agreement with earlier work on water-soluble hydrate formers (Wilson et al. 2005; Wilson and Haymet, 2008). However, more work is needed before the current nucleation criterion in CSMHyK can be improved. The experiments presented here were all performed with small non-sheared systems with minimal solid impurities. In the case of the flowloop experiments described in Chapter 7, much lower subcoolings were required for hydrate nucleation (See Figure 7.11). More work is needed to understand the most important parameters that lead to these contrasting results before a qualitative correlation can be proposed. Such work may also lead to improved hydrate prevention measures by reducing the probability of hydrate nucleation at a given subcooling. The minimum subcooling criterion that was required for hydrate nucleation in this work was 20°C. If this could be achieved in a flow line, it could lead to large reductions in the use of thermodynamic hydrate inhibitors.

4.6 Conclusions

The key findings from Chapter 4 are as follows:

1. The probability of hydrate nucleation increases to close to 100% within a narrow band of subcooling of within three degrees for both methane/water and xenon/water systems. Experimentally this effect is manifested as a transition from stochastic to deterministic behavior as subcooling is increased.

2. At lower subcoolings, the nucleation is more stochastic but the time distribution of hydrate nucleation becomes narrower as the subcooling is increased.
3. Further experimental investigation is required in order to develop realistic probabilistic distributions for nucleation events in industrial systems.
Chapter 5

STUDIES OF THE MASS TRANSFER MECHANISMS FOR HYDRATE FILM GROWTH USING RAMAN SPECTROSCOPY

Due to the availability of hydrate formers, gas hydrates tend to form first at interfaces between a phase rich in the host molecule, typically water, and a phase rich in the guest molecule such as methane, ethane or CO$_2$. The rate of hydrate formation at such interfaces is rapid and leads to the formation of a film which separates the two phases and retards the hydrate formation rate (Sloan and Koh 2008). In systems where no such interface exists such as in some natural hydrate deposits, hydrate formation occurs from saturated phases in a process that can take months or years (Spangenberg et al. 2005).

The formation of hydrate films at guest-host interfaces has been observed for hydrate formation from water-hydrocarbon interfaces (Maini et al. 1981; Servio and Englezos 2003; Taylor et al. 2008), CO$_2$-water interfaces (Teng et al. 1996; Hirai et al. 1996; Uchida et al. 1999; Uchida et al. 2002; Servio and Englezos 2003; Katsuki et al. 2006), water-fluorocarbon interfaces (Ohmura et al. 2000; Kobayashi et al. 2001; Sakaguchi et al. 2003), on the surface of ice particles (Staykova et al. 2003; Moudrakovski et al. 2004; Kuhs et al. 2006), and on emulsified water droplets (Moudrakovski et al. 2004). Once the hydrate film has formed across the interface, the hydrate film can thicken due to the diffusion of guest molecules initially dissolved inside the host-rich phase, and host molecules initially dissolved in guest-rich phase. However, at longer timescales when the dissolved hydrate formers become depleted,
the hydrate formation rate is limited by the mass transfer of the hydrate formers across the hydrate film. A conceptual picture for the development of a hydrate film around water droplets entrained in the oil phase is presented in Figure 3.2.

The formation of a hydrate film across an interface between a guest-rich phase and a host-rich phase has been studied in detail by a number of researchers. Studies have been reported for both CO₂-water systems (Uchida et al. 1999; Mori, 2001; Mochizuki and Mori 2008) and for methane-water systems (Taylor, 2006; Freer et al. 2001). The growth rate has been shown to be limited by heat or mass transfer between the growing hydrate film front and the bulk fluid phases. Mochizuki and Mori provided a summary of the various heat transfer models (Mochizuki and Mori 2005), and later proposed a similar mass transfer model (Mochizuki and Mori 2008). The rate of hydrate film growth is very rapid: from 20 to 1000 μm/s (Freer et al. 2001; Uchida et al. 1999; Uchida et al. 2002), and for most industrial applications the formation rate of this film will be effectively instantaneous compared to the length of the simulation. However, an understanding of the subsequent growth resulting from the mass transfer of hydrate formers across the film will be of great importance for making accurate predictions of hydrate formation rates in industrial scale systems.

There is some controversy about whether it is the transport of the guest (Makogon 1981; Teng et al. 1996; Hirai et al. 1996; Henning et al. 2000; Wang et al. 2002; Moudrakovski et al. 2004), or the host molecule (Topham et al. 1984; Shindo et al. 1995; Mori and Mochizuki 1996; Sugaya and Mori 1996; Mori and Mochizuki 1997; Mochizuki and Mori 2000) across the film that controls the hydrate growth rate. This question has notable importance since it determines the driving force for hydrate formation and how well the model will transfer between different systems. If the mass transfer of the guest molecule across the hydrate film controlled the hydrate
formation rate then one might expect that a higher concentration of methane in the hydrocarbon phase would lead to a faster rate of hydrate formation, but this would not be the case if it were the host molecule that was controlling the hydrate formation rate. In addition, the mobility of the host molecule through the hydrate film might have implications for particle agglomeration which has been shown to be promoted by free water on the particle’s surface (Taylor, 2006); if unconverted water inside of the hydrate film were able to escape to the surface of a particle, it could lead to increased aggregation. This would be a particular concern if hydrate formation were in a heat transfer limited regime where the water could migrate to the surface of a hydrate particle without converting to hydrate.

It is the aim of this study to better understand the mass transfer mechanism across a hydrate film in order to explicate the quantitative growth rate measurements that are described in Chapter 6. Section 5.1 of this chapter describes the previous attempts that have been made to study the mechanisms for mass transfer across a hydrate film. Section 5.2 describes a new method that was developed in this work to study the mass transfer mechanism using isotopic tracers. Section 5.3 shows the results that were collected from this new method, and Section 5.4 describes the key conclusions from this chapter.

5.1 Previous Attempts to Elucidate the Mass Transfer Mechanisms Across Hydrate Films

Since ice Ih is composed of a hydrogen-bonded water lattice, it is often used as an analogy to hydrate. The mass transfer mechanisms of water and gas molecules within ice Ih have been studied in detail by a number of researchers and are well understood. There is a general agreement that the diffusion of gas molecules in ice Ih is dependent
on the molecular radii of the gas molecules with smaller molecules diffusing faster than larger molecules. The diffusivities of helium, neon and argon in ice Ih have been measured at $10^{-9}$, $10^{-10}$, and $10^{-11}$ m$^2$/s respectively, at temperatures between -15 and -5°C (Satoh et al. 1996). The diffusivities of molecular nitrogen and oxygen in ice Ih were estimated at $10^{-13}$ m$^2$/s at -10°C (Ikeda et al. 1999). The diffusivity of methane in ice was estimated at $10^{-13}$ m$^2$/s at -5°C by modeling experimental results of hydrate dissociation (Komai et al. 2004) and similar estimates for the diffusivity of CO$_2$ in ice gave a value of $10^{-12}$ m$^2$/s at -5°C (Uchida et al. 2003). Predictions of the diffusion of gas molecules in ice Ih using the molecular orbital method gave similar values; the diffusivity of oxygen, nitrogen and methane in ice were predicted to be $10^{-11}$, $10^{-12}$ and $10^{-14}$ m$^2$/s respectively (Hori and Hondoh 2003).

In all cases, the diffusion of gas molecules in ice Ih was found to be much higher than the diffusion of water. The self diffusion coefficient of water in ice was found to be highly sensitive to temperature. At temperatures between -50°C and 0°C, the self diffusion coefficient was found to be between $10^{-16}$ to $10^{-15}$ m$^2$/s (Goto et al. 1986). At lower temperatures, the self diffusion coefficient was found to be even lower: between $10^{-20}$ and $10^{-18}$ m$^2$/s at temperatures between -133°C and -103°C (Livingston et al. 1998; Livingston et al. 2002; Oxley et al. 2006).

Based on the findings for ice, one might expect that gas molecules would also diffuse faster than water molecules in hydrate. However, the mechanisms for the diffusion of gas and water molecules in ice are quite different. Molecular dynamics simulations of water and helium diffusion in ice Ih have shown that interstitial water molecules diffuse by distorting the water lattice, whereas helium hops from one site to the next through hexagonal rings (Ikeda-Fukazawa et al. 2002). In the case of sI hydrate, a molecule diffusing from one large cage to another through hexagonal rings
would be retarded if an adjacent cage were already occupied by a guest molecule. This would result in a lower diffusion rate of gas in hydrate compared to ice since the diffusion rate in solids is proportional to the number of free sites (Borg and Dienes, 1988). Estimates based on hydrate formation rate from ice particles place the diffusivity between $10^{-17}$ and $10^{-16} \text{m}^2/\text{s}$ although it was not clear if this were due to the diffusion of water or methane in the hydrate (Staykova et al. 2003; Kuhs et al. 2006).

A number of experimentalists have studied the relative mass transfer rates of guest and host molecules in hydrate. It was noted that CO$_2$ hydrate forms faster than methane hydrate under the same fugacity driving force which might indicate that the diffusion of the guest molecule is responsible for the hydrate growth; the apparent gas-water diffusion coefficient for methane hydrate was found to be approximately $10^{-16} \text{m}^2/\text{s}$ and was three times faster for CO$_2$ hydrate at $10^{-15} \text{m}^2/\text{s}$ (Staykova et al. 2003). However, by regressing a number of parameters to experimental data using some constraints, Salamantin et al. (1998) suggested that air molecules diffuse through hydrate ten times slower than water, but that their diffusion rate is still significant.

The modeling community have also taken an interest in this question. Monte Carlo simulations have suggested that the diffusivity of CO$_2$ in hydrate was much higher than water in hydrate: $10^{-12} \text{m}^2/\text{s}$ for CO$_2$ at 0°C compared to $10^{-23} \text{m}^2/\text{s}$ for water at -73°C (Demurov et al. 2002). In addition, recent kinetic Monte Carlo equilibrium path sampling also suggested that guest molecules diffuse faster than water molecules in sI hydrate, a diffusivity of $10^{-16} \text{m}^2/\text{s}$ was obtained for methane in sI hydrate (Peters et al. 2008).

Scanning Electron Microscope images of hydrates have shown them to be meso-
porous. Pores would significantly increase the mass transfer rate across a hydrate film compared to the solid plates that are assumed in the molecular simulations. The pores have been shown to fill over time, making the hydrate more dense. (Stern et al. 2004; Stern et al. 2005). The pores range in size from 100 nm to 1 \( \mu m \) (Kuhs et al. 2004) and despite the water-wet nature of the hydrate (Hirata and Mori 1998), the pores are filled with gas (Kuhs et al. 2004). The porous structure will likely depend on the hydrate formation conditions. In the case of ice, the pores that form from shock cooled brine tend to be larger (up to 300 \( \mu m \)), than for ice formed under controlled conditions (up to 50 \( \mu m \)) (Menzel et al. 2000).

5.2 The Application of Isotopic Tracers and Confocal Raman Spectroscopy to Probe the Mass Transfer Mechanics

In this study, Raman spectroscopy was used to study the mass transfer of methane and water across a hydrate film in order to determine whether the diffusion of water or gas is responsible for the growth of the hydrate film. A methane hydrate film was formed at a gas-water interface from \( CH_4 \) and \( H_2O^{16} \). A tracer was then added to the vapor or water phase. The concentration profile of the tracer in the hydrate was then monitored as a function of time using either the peak area ratio in the case of the vapor-based tracer, or the peak position in the case of the water-based tracer. It has previously been demonstrated that the Peak-Area-Ratio (PAR) method can be used to determine the concentration of dissolved methane in water under pressurized conditions (Lu et al. 2008). The PAR method was also shown to give reliable values for the diffusivity of dissolved methane in water under pressurized conditions. (Lu et al. 2006).
5.2.1 A Description of the Confocal Raman Spectrometer.

A confocal Raman spectrometer was used for these experiments to allow the tracer concentration to be measured as a function of time and position in the hydrate film. The confocal Raman spectrometer also allowed images of the hydrate film to be recorded to observe morphological changes as the film annealed over time. A schematic of the principle behind a Raman spectrometer was provided by Strobel (2007) and is shown in Figure 5.1.

The confocal Raman spectrometer used was a Horiba Jobin Yvon LabRamHR with a 20x objective lens. The excitation source was provided by a diode laser with a wavelength of 532.08 nm. Scattered light from the sample was passed through an entrance slit that was typically set at 100 μm, and was then dispersed by a grating with a density of 1800 grooves/mm. The focal length for the spectrometer was 800 mm. The spectrometer was calibrated using neon emission lines and the resolution of the spectrometer was less than 1 cm$^{-1}$. The spectra were analyzed using Grams/AI version 7.02 from Thermo Galactic Inc.
5.2.2 Experimental Setup and Procedures.

The experimental setup for the vapor and water replacement experiments are shown in Figures 5.2 and 5.3. The hydrate film was formed inside a high pressure cell which was custom made by *Sam O. Colgate Inc.* The cell had a pressure rating of 350 bar and a volume of 1 cm$^3$. First, deionized water was loaded into the cell using a glass syringe. The volume of water added to the cell for the vapor replacement experiments was critical: too little and the resultant hydrate film would consume most of the water phase and would be difficult to measure; too much and hydrate would block the two gas-filled ports located half way up the cell. A water volume of 0.3 cm$^3$ was found to be optimal for these experiments.

For the water replacement experiments, the setup was modified as shown in Figure 5.3 (right). Avoiding the blockage of the two ports in these experiments was more complicated since the hydrate film would need to be formed above the ports to allow the water phase to be replaced. In addition, pressurizing the cell with gas introduced a problem since the line used for gas charging was still filled with gas that was in contact with water. This line would inevitably plug with hydrate when the cell was cooled.

To avoid this problem, a small volume of water was displaced into the line before hydrate formation. This was achieved by filling an adjacent piece of tubing, 8 cm in length and 0.3175 cm (1/8 inch) diameter with H$_2$O$^{18}$ water at the same time as the cell was filled. The gas would be charged through the other port and once charged, 1 cm$^3$ of water would be displaced from the tubing, through the cell, into the line that had been used for gas charging. The cell was filled with a water volume of approximately 0.7 cm$^3$ for the water replacement experiments. Prior to the water replacement experiments, 3 cm$^3$ of the H$_2$O$^{18}$ water had been loaded into another
piece of tubing, 8 cm in length and 0.635 cm (1/4 inch) in diameter. The two pieces of tubing were connected in parallel by two three way valves which allowed either tube to be used to displace the water in the cell. Once the hydrate film had been formed and annealed, the three way valves would be opened to the H$_2$O$^{\delta 18}$ water and the water was slowly displaced. The total volume of water replaced was 3 cm$^3$. This ensured the effective replacement of the H$_2$O$^{\delta 16}$ water beneath the hydrate film with H$_2$O$^{\delta 18}$ water. Both the vapor replacement and the water experiments were challenging. The inlet and outlet ports would frequently plug with hydrate and estimating the water volume added to the cell was also difficult.

Once concern with these experiments is that the H$_2$O$^{\delta 18}$ would not be saturated with methane before it was used in the replacement experiments. Although the H$_2$O$^{\delta 18}$ water was pressurized with the hydrate forming gas for 24 hours before it was added to the cell, this would not be enough time to allow complete saturation of the water with the hydrate former. Therefore, it was possible that replacing the water phase with under saturated water would cause partial dissociation of the hydrate. Avoiding this problem would be difficult because if the water phase were allowed to equilibrate with the hydrate forming gas at room temperature prior to the experiment, it would then be oversaturated with the hydrate former when in contact with the hydrate phase (Subramanian, 2002), this would lead to additional hydrate formation. In order to pre-saturate the H$_2$O$^{\delta 18}$ with the same concentration of dissolved methane as in the water layer beneath the hydrate, the H$_2$O$^{\delta 18}$ would need to be presaturated with methane at 70 bar and 30°C as shown in Figure 5.4. Pre-saturating the water in a reasonable timescale would also require agitation. This would require significant modifications to the apparatus.

To determine if it was necessary to pre-saturate the water phase with methane, a
calculation was performed to determine the maximum extent of hydrate dissociation that would be expected if the aqueous phase were completely replaced with unsaturated H$_2$O$^{\delta_{18}}$. The original aqueous phase would be in equilibrium with the hydrate film at 4°C and would have a dissolved methane mole fraction of 0.0014 according to Figure 5.4. This corresponded to 5.3x10$^{-5}$ moles of methane initially dissolved in the aqueous phase which had a volume of 0.7 cm$^3$. If the water phase was replaced with unsaturated H$_2$O$^{\delta_{18}}$ then 5.3x10$^{-5}$ moles of methane would need to dissolve in the aqueous phase to re-establish equilibrium between the aqueous and hydrate phases.

For a non-porous hydrate film 1000$\mu$m thick covering the water surface (1 cm wide and 1.65 cm deep), approximately 1.2x10$^{-3}$ moles of hydrated methane would be available to dissolve in the water phase. In this scenario, a maximum of 4% of the hydrate film would need to dissolve to re-saturate the aqueous phase with methane. Thus the problem of water saturation is considered negligible for these experiments.

When replacing the water or the vapor phase in the cell, it was essential to avoid changes in pressure within the system. Such changes were found to lead to the cracking of the hydrate film. Such pressure changes were avoided using a Ruska Tandem Pump that was loaned to CSM by Walter Chapman at Rice University. The Tandem Pump consisted of two gas cylinders, each with a volume of 100 cm$^3$, connected by a piston which ensured that the total volume of the two cylinders was conserved as the piston was moved. The pump can provide flow rates from 2.5 to 560 cm$^3$/hr to an accuracy of within 0.5 cm$^3$/hr.

For the vapor replacement experiments, the tracer gas was added to one of the cylinders and the hydrate former to the other. Once the hydrate had formed the tandem pump could then be used to displace the vapor phase in the cell with the tracer gas without affecting the pressure. In the case of the water replacement experiments,
both of the cylinders were filled with the hydrate forming gas and the \( \text{H}_2\text{O}^{\delta18} \) water was added to the cell by displacing the water from the 0.635 cm (1/4 inch) diameter tubing into the cell.

Temperature in the Raman cell was controlled by a circulating cooler (1167P from VWR). The cooler was mounted on a trolley which allowed it to be moved. Once the gas or water had been replaced, the cell was isolated using two needle valves, and the associated piping was vented. The cell was disconnected using two quick connects and the cell and cooler assembly were moved to the confocal Raman spectrometer where it was mounted on an (x-y-z) stage.

The protiated methane and carbon dioxide used for these experiments was provided by General Air Inc. at 99.97 mol% and 98.8 mol% respectively. The isotopic tracers: CD\(_4\), CHD\(_3\) and H\(_2\text{O}^{\delta18}\) were provided by Cambridge Isotopes Inc. at purities of 99 mol%, 98 mol% and 97 mol% respectively.

For the gas replacement experiments, a single acquisition of 60 seconds was used. For the water replacement experiments, three acquisitions of 100 seconds were used to capture the lattice vibrational mode of the hydrate.

### 5.3 Results from the Isotope Replacement Experiments

The confocal ability of the Raman spectrometer allowed microscopic images of the hydrate film to be acquired. Figure 5.5 shows a set of images of a methane hydrate film that were taken soon after the hydrate film formed at 4°C and 70 bar. The gas phase shows up as a light color and the hydrate appears dark. The figures clearly show gas filled pores in the hydrate and over time the pores fill with hydrate.
Figure 5.2. A Schematic of the Experimental Setup for the Gas Replacement Experiments

Figure 5.3. A Schematic of the Experimental Setup for the Gas Replacement (Left) and Water Replacement Experiments (Right)
Figure 5.4. A Plot Showing the Predicted Equilibrium Aqueous Phase Concentration as a Function of Temperature Before and After Hydrate Formation at 70 bar (Multiflash CPA Association Model)
Figure 5.5. Confocal Microscope Images of the Hydrate Film Showing Pore Filling: 0 Minutes (Top Left), 10 Minutes (Top Right), 20 Minutes (Lower Left), 30 Minutes (Lower Right)
5.3.1 CO₂ Replacement Experiments

Prior to moving to costly isotopic tracers, the experimental procedure was tested and refined using carbon dioxide, a readily available gas in the laboratory. Coincidentally, the replacement of methane in naturally occurring hydrate sediments with carbon dioxide is of importance to a number of researchers (Ohgaki et al. 1996; Hirohama et al. 1996; Jadhawar et al. 2005; Graue et al. 2006; Stevens et al. 2008; Husebø et al. 2008) who are interested in sequestering the greenhouse gas while recovering methane as a fuel source. Carbon dioxide is a more stable hydrate former than methane and hence there is a thermodynamic driving force for the CO₂ to be enclathrated at the expense of the methane, but the kinetics of the replacement can be quite slow (Jadhawar et al. 2005). Since CO₂ has a low vapor pressure, it was necessary to perform the CO₂ replacement experiments at lower pressures to prevent a phase change occurring when the two components: methane and carbon dioxide were mixed. Such a phase transition from mixing could lead to rapid increases in pressure (Hughes, 2004). The experiments were performed at a pressure of 27.6 bar and a temperature of 0.1°C.

The carbon dioxide molecule has two Raman bands see Figure 5.6. The peaks overlapped for CO₂ in the gas and hydrate phases, but the hydrate phase peak was much broader which allowed the peaks to be deconvoluted. The peak positions for CO₂ are 1286 and 1389 cm⁻¹ in the gas and 1277 and 1382 cm⁻¹ in the hydrate phase (Sum, 1996). This is too far away from the methane symmetric stretch at 2915 cm⁻¹ to be observed with the same grating position. The grating would need to be realigned between observing the methane and the CO₂ peaks which could lead to a different relative intensity of the peaks, making quantification of the molar compositions unreliable. A lower density grating would have increased the range of the
Figure 5.6. Example Raman Spectra 200 μm from the Top of the Hydrate Film (Left) and 800 μm from the Top (Right) 3 Hours after the CO₂ Replacement

wavenumbers that could be observed but would greatly reduce the resolution of the peaks (Strobel, 2008). Since the aim of these preliminary CO₂ experiments is mainly qualitative in nature, these limitations were not a problem here. However, it would be an issue if quantitative information were required.

The results from the CO₂ replacement experiments are shown in Figure 5.7. Each point on the plot shows the peak area ratio of CO₂ to methane in the gas and hydrate phases as a function of distance from the top of the hydrate film at different times after the gas phase had been replaced. Prior to the gas replacement, the film had only been annealed for one hour. The top of the hydrate film contained a large contribution from CO₂ almost immediately after the gas phase had been replaced. Initially, little CO₂ was present in the rest of the film, but over time the CO₂ content increased further into the film.

Figure 5.6 shows two spectra of the CO₂ contribution at approximately 3 hours after the gas phase was replaced; the left spectrum was taken towards the top of the hydrate film and the right spectrum was taken further in to the film. The signal from the gaseous CO₂ decreased relative to the enclathrated CO₂ further in to the film,
Figure 5.7. The Peak-Area-Ratio of CO$_2$ to CH$_4$ as a Function of Distance from the Top of the Hydrate Film for Various Times after the CO$_2$ Replacement indicating that the CO$_2$ was being incorporated into the hydrate as it moved through the film.

### 5.3.2 CD$_4$ Replacement Experiments

Figure 5.8 shows an example Raman spectrum for deuterated methane gas (CD$_4$) which was taken using a 60 second acquisition. The spectrum shows several peaks that are highly convoluted. The measured positions of the peaks agree well with literature values determined by Bermejo et al. (1977) at 1.5 bar. There are two problems with using CD$_4$ for the gas phase tracer: firstly, the position of the peaks is too far away from the symmetric stretch of CH$_4$ to see both with the same grating
Figure 5.8. Example Raman Spectra for the Gas Phase of $\text{CD}_4$ at 4°C and 70 bar Showing the Peak Positions Assigned by Bermejo et al. (1977)

position; secondly, the convolution of the peaks will make it difficult to accurately measure the peak area, particularly for low $\text{CD}_4$ concentrations where it would be difficult to resolve the smaller peaks.

### 5.3.3 CHD$_3$ Replacement Experiments

An alternative to $\text{CD}_4$ is CHD$_3$. The peak positions and intensities for the gas phase of this molecule were also measured by Bermejo et al. (1977) at 1.5 bar, as were CH$_3$D and CH$_2$D$_2$. Of these molecules, CHD$_3$ was found to be the most suitable gas phase tracer since it has an asymmetric stretching mode that is sufficiently far away
from the symmetric stretching mode of CH$_4$ to allow both peaks to be resolved, but the peaks are close enough together to allow both to be viewed with the same grating position. In addition, the intensity of the asymmetric stretching mode is quite high which means that the tracer could be detected in low concentrations.

Typical Raman spectra for the gas phases of CH$_4$ and CHD$_3$ at 4°C and 70 bar are shown in Figure 5.9. The $\nu_{3a}(a_1)$ asymmetric stretch of CHD$_3$ is separated from the symmetric stretch of CH$_4$ by approximately 75 wavenumbers, but has only 35% of the intensity. A typical Raman spectrum of a binary hydrate of CH$_4$ and CHD$_3$ is shown in Figure 5.10. The relative intensities of CH$_4$ in the large and small cages are quite similar, suggesting some gas phase contribution to the small cage peak intensity. The spectrum also shows that the asymmetric stretch of the CHD$_3$ molecule also splits into two peaks in the presence of hydrate which is probably due to the different environments of the large cage of sI hydrate and the small cage or vapor phase.

The clear separation of the peaks for CHD$_3$ in the gas and hydrate phases allowed for calibration curves to be constructed to relate the ratio of the CH$_4$ and CHD$_3$ peak areas to the ratio of the mole fractions for the vapor and hydrate phases using known gas compositions. Calibration curves were constructed for both the vapor and hydrate phases using the peak at 2979 cm$^{-1}$ to represent the hydrate phase and the peak at 2990 cm$^{-1}$ to represent the vapor phase. The contribution of the small cage to the peaks was neglected in the construction of these calibration curves due to the difficulty deconvoluting the peak. The calibration curves for the vapor and hydrate phases are shown in Figures 5.11 and 5.12 respectively. The calibration curves allowed the molar concentrations of the gas and hydrate phases to be determined from the peak area ratios that were measured in the gas replacement experiments. It was assumed for
Figure 5.9. Example Raman Spectra for the Gas Phase of CHD$_3$ Compared to CH$_4$ at 4°C and 70 bar Showing the Peak Positions Assigned by Bermejo et al. (1977)
Figure 5.10. Example Raman Spectra for a Mixed Gas Hydrate of CHD$_3$ and CH$_4$ with Some Vapor Phase Contribution at 4°C and 70 bar
Figure 5.11. A Calibration Curve Relating the Peak-Area-Ratio of CH$_4$ to CHD$_3$ to the Mole Fraction of CH$_4$ in the Vapor Phase at 4°C and 70 bar

these experiments that the hydrate had no preference for the protiated methane CH$_4$ or the tracer CHD$_3$. In the literature a small preference of the hydrate for protiated methane has been reported (Hachikubo et al. 2008), however the difference between the composition of the vapor and hydrate phases was less than 5 mol% at 1°C.

Figures 5.13 to 5.16 show the tracer concentrations that were measured in the vapor and hydrate phases as a function of distance from the hydrate film at different times after the gas phase had been replaced for four different experiments. Each point in the figures represents an average of five measurements at different horizontal positions within the hydrate film; each measurement was made using a 60 second acquisition time. The typical standard deviation for a set of five measurements was
Figure 5.12. A Calibration Curve Relating the Peak-Area-Ratio of CH\textsubscript{4} to CHD\textsubscript{3} to the Mole Fraction of CH\textsubscript{4} in the Hydrate Phase at 4°C and 70 bar
In the first experiment, the hydrate film was formed at 70 bar and 4°C and the vapor phase was replaced soon after the film had nucleated. The results from this experiment are shown in Figure 5.13. It is clear from the mole fractions of tracer that were measured that the vapor was highly mobile within the hydrate film but that the concentrations of CHD$_3$ measured in the hydrate phase was much lower. Over time, more of the tracer became incorporated into the hydrate phase with the greatest concentration towards the top of the hydrate film. This was later attributed to the filling of gas-filled pores within the hydrate that were more prevalent towards the top of the hydrate film.

In the second experiment, the hydrate film was allowed to anneal for 24 hours before the vapor phase was replaced. This ensured that most of the pore filling had occurred prior to the addition of the tracer to avoid pore filling contributing to the results. The results for the second experiment are shown in Figure 5.14. Again, the composition of the tracer in the gas phase rapidly increased to the bulk gas phase composition, indicating the high mobility of the gas phase within the hydrate film. However, in this case much less tracer was incorporated into the hydrate, even 84 hours after the tracer had been added. This result suggested that the increase in the concentration of CHD$_3$ in the hydrate phase that was observed in the first experiment were due to pore filling. Towards the end of the second experiment, the concentration of CHD$_3$ in the hydrate at the top of the hydrate film started to increase. This increase was either caused by the formation of new hydrate formed due to water permeation through the hydrate film, or from the diffusion of gas molecules through the hydrate lattice.

The results obtained in these experiments showed no dependence on the sys-
Figure 5.13. The Mole Fraction of CHD₃ in the Vapor (Left) and the Hydrate (Right) as a Function of Distance from the Top of the Hydrate Film for Various Times after the Gas Replacement for a Non-Annealed Hydrate Film Formed at 4°C and 70 bar

tem pressure: the results from hydrate films formed at 70, 103 and 140 bar were qualitatively similar as shown in Figures 5.14, 5.15 and 5.16 respectively.

5.3.4 H₂O¹⁸ Replacement Experiments

In order to provide complementary evidence for the mass transfer mechanism, experiments were performed where the water phase beneath a hydrate film was replaced by an isotopic tracer. The isotopic tracer chosen for these measurements was H₂O¹⁸. In the literature, it has been shown that H₂O¹⁶ and H₂O¹⁸ diffuse at the same rate in ice Ih (Livingston et al. 1997), it is therefore assumed that both would behave similarly in a hydrate lattice. In addition, the diffusion rate of helium in
Figure 5.14. The Mole Fraction of CHD₃ in the Vapor (Left) and the Hydrate (Right) as a Function of Distance from the Top of the Hydrate Film for Various Times after the Gas Replacement for a Hydrate Film which was Formed at 4°C and 70 bar and Annealed for 24 Hours Before the Gas Replacement
Figure 5.15. The Mole Fraction of CHD₃ in the Vapor (Left) and the Hydrate (Right) as a Function of Distance from the Top of the Hydrate Film for Various Times after the Gas Replacement for a Hydrate Film which was Formed at 4°C and 103 bar and Annealed for 24 Hours Before the Gas Replacement.
Figure 5.16. The Mole Fraction of CHD$_3$ in the Vapor (Left) and the Hydrate (Right) as a Function of Distance from the Top of the Hydrate Film for Various Times after the Gas Replacement for a Hydrate Film which was Formed at 4°C and 140 bar and Annealed for 24 Hours Before the Gas Replacement
ice Ih formed from H$_2$O$^{\delta 16}$ and H$_2$O$^{\delta 18}$ was found to be similar (Daschbach et al. 2004). One disadvantage of using H$_2$O$^{\delta 18}$ as a tracer is that hydrate has been shown to concentrate the H$_2$O$^{\delta 18}$ by up to 0.3%, (Davidson et al. 1983; Maekawa, 2004; Maekawa and Imai, 2000), this might have a slight impact on the results. The hydrate equilibrium temperature was shown to have no measurable dependence on the H$_2$O$^{\delta 18}$ concentration. The sI hydrate phase equilibrium line for methane CH$_4$ and water H$_2$O$^{\delta 18}$ is shown in Figure 5.17. The data was collected in the high pressure DSC, described in Chapter 4. The hydrate phase boundary for the enriched water coincided with the CSMGem prediction for CH$_4$ and water H$_2$O$^{\delta 16}$.

An alternative to the H$_2$O$^{\delta 18}$ would have been deuterated water - D$_2$O. The
diffusion rate of deuterated water and H$_{2}$O$^{518}$ in ice Ih have been shown to be similar at the temperatures of interest (Kuhn and Thürkauf 1958). However, deuterated water has more disadvantages than H$_{2}$O$^{518}$. Firstly, at temperatures below -73°C, D$_{2}$O diffuses faster in ice Ih than H$_{2}$O (Bartels et al. 1992), it is therefore unclear how the diffusion rates would compare in a hydrate lattice. Secondly, the diffusion rate of helium in D$_{2}$O ice was shown to be higher than in H$_{2}$O ice due to the lower vibrational frequency of the O-D bond which allows for easier hopping of the gas molecule from site to site (Daschbach et al. 2004). Additionally, hydrates have been shown to concentrate D$_{2}$O to a greater extent than H$_{2}$O$^{518}$, as much as 2.2% (Maekawa, 2004; Maekawa and Imai, 2000). Finally, methane hydrate formed from D$_{2}$O has an equilibrium temperature that is higher than H$_{2}$O methane hydrate by approximately 2.5°C (Buchanan et al. 2005).

The lattice vibrational mode of ice Ih has been shown to depend on the concentration of O$^{518}$ in the lattice. The frequency decreases as the concentration of O$^{518}$ increases. The shift in the vibrational frequency for H$_{2}$O$^{518}$ and H$_{2}$O$^{516}$ is between 5 and 30 wavenumbers, but the peaks are quite broad (Gompertz and Orville-Thomas 1959). Raman spectra of ice Ih for three different O$^{518}$ concentrations are shown in Figure 5.18. Each spectrum was recorded using five acquisitions, each of 60 seconds.

The measured lattice vibrational mode for hydrate also depends on the O$^{518}$ concentration. The spectra shown in Figure 5.19 are for methane hydrate formed from H$_{2}$O$^{516}$ and H$_{2}$O$^{518}$ at 70 bar and 4°C. The spectra were taken using 5 acquisitions, each of 60 seconds. As with the lattice vibrational frequencies for ice Ih, the lattice vibrational frequencies for sI methane hydrate also shift to lower frequencies as the O$^{518}$ concentration is increased, but the peaks are much broader than for ice Ih. The shift in the lattice vibrational frequency of sI methane hydrate as a function of O$^{518}$
Figure 5.18. The Effect of the Concentration of $O^{\delta_{18}}$ on the Lattice Vibration of Ice Ih
Figure 5.19. The Effect of the Concentration of $^{18}$O on the Lattice Vibration of sI Methane Hydrate at 4°C and 70 bar

concentration is shown in Figure 5.20. As expected, the lattice vibrational frequency shifts linearly with the $^{18}$O concentration. Figure 5.20 can be used as a calibration curve to determine the $^{18}$O concentration in the hydrate film from the measured lattice vibrational frequency.

The results from a water replacement experiment are shown in Figure 5.21. The error bars on the plots represent a measurement uncertainty of ±1 wavenumbers. The methane hydrate film was formed at 70 bar and 4°C and allowed to anneal for 24 hours before the water phase was replaced. The concentration of the bulk water phase was determined at the end of the experiment from the lattice vibrational frequency of ice that was formed by depressurizing the cell and freezing the water phase.
Figure 5.20. A Calibration Curve Relating the Lattice Vibration to the Mole Fraction of $\text{H}_2\text{O}^{\delta 18}$ in the Hydrate Phase at 4°C and 70 bar

$y = -17.5x + 214.7$
Figure 5.21. The Mole Fraction of $H_2O^{518}$ in the Hydrate Lattice as a Function of Distance from the Top of the Hydrate Film for Various Times after the Water Replacement for a Hydrate Film which was Formed at $4^\circ$C and 70 bar and Annealed for 24 Hours Before the Water Replacement.
The results from the water replacement experiments suggest that the water molecule is highly mobile within the hydrate film. The first set of measurements was taken 1 hour after the water phase had been replaced. The results showed that the O$^{18}$ concentration was increasing with distance from the top of the hydrate film. The top of the hydrate contained very little O$^{18}$, but the concentration of O$^{18}$ in the hydrate at the bottom approached that of the bulk water phase. Within 24 hours, the concentration of O$^{18}$ in the hydrate phase approached that of the bulk water. The water replacement experiment was repeated since in the original experiment, most of the changes were observed within the first 24 hours after the water phase had been replaced. In the repeat experiment, spectra were taken at much shorter intervals in an effort to better quantify the rate of movement of the water molecules within the hydrate. The results for the repeat experiment are shown in Figure 5.22. Again, the water molecules appeared highly mobile. After 24 hours, the concentration of tracer in the hydrate film approached that of the bulk water.

The apparent mobility of the water molecules within the hydrate films was startlingly high. Previous estimates of the diffusivity of hydrate formers in hydrate are between $1\times10^{-17}$ and $1\times10^{-15}$ m$^2$/s (Staykova et al. 2003; Kuhs et al. 2006). Treating the hydrate film as a flat plate and applying the one-dimensional Fickian diffusion model described in Section 6.3, little movement of the hydrate formers through a hydrate film would be expected in the first 24 hours based on an effective diffusivity of $1\times10^{-16}$ m$^2$/s (See Figure 5.23). Further, the effective diffusivity would need to be increased to $1\times10^{-13}$ m$^2$/s for a similar trend in the hydrate former mobility in a 24 hour period (See Figure 5.24).

The unexpectedly high mobility of the water molecules that was observed in these experiments suggests a problem with the experimental method. One explanation is
Figure 5.22. A Repeat Experiment Showing The Mole Fraction of H₂Oδ₁⁸ in the Hydrate Lattice as a Function of Distance from the Top of the Hydrate Film for Various Times after the Water Replacement for a Hydrate Film which was Formed at 4°C and 70 bar and Annealed for 24 Hours Before the Water Replacement.
Figure 5.23. The Expected Concentration of the H$_2$O$^{618}$ in the Hydrate Film as a Function of Time Based on an Effective Diffusivity of $1 \times 10^{-16}$ m$^2$/s
Figure 5.24. The Expected Concentration of the H$_2$O$^{\delta 18}$ in the Hydrate Film after 24 Hours as a Function of Effective Diffusivity
that wall effects caused the water molecules to be preferentially mobile along the interface between the hydrate film and the window. This would bias the results of Raman spectra taken close to the window. This problem could be mitigated by designing a new Raman cell with a window located at the top. Raman spectra could then be taken from above, adjusting the focal point of the laser to obtain a tracer concentration profile as a function of depth.

5.4 Conclusions

The key conclusions for Chapter 5 are as follows:

1. Water molecules appeared to be more mobile than methane molecules within a hydrate film, however further experimental studies are needed to ensure that wall effects are mitigated.

2. CHD$_3$ is a good tracer for the gas phase since its composition within the hydrate can be monitored with Raman spectroscopy using the ratio of the symmetric stretch of CH$_4$ to the asymmetric stretch of CHD$_3$, both can be observed with the same grating position.

3. H$_2$O$^{618}$ is a good tracer for the water phase since its composition within the hydrate can be monitored with Raman spectroscopy using the lattice vibrational mode.
Chapter 6

HYDRATE FILM GROWTH RATES IN A HIGH PRESSURE DIFFERENTIAL SCANNING CALORIMETER

Once a hydrate film has completely formed across an interface between a phase rich in guest molecules and a phase rich in host molecules, further hydrate growth is mass transfer limited. Guest molecules initially dissolved in the water phase can migrate to the hydrate film, as can water that was initially dissolved in the guest-rich phase. However, at longer timescales when the dissolved hydrate formers become depleted, the hydrate formation rate is limited by the mass transfer of the hydrate formers through the hydrate film. The confocal Raman spectroscopy studies that were described in Chapter 5 suggested that the rate of mass transfer across a hydrate film is predominantly controlled by the movement of water molecules. These measurements were mechanistically insightful, but were unable to provide quantitative information on the rate of mass transfer due to the small amount of data that was collected.

The mass transfer of hydrate formers across a hydrate film has been of interest to a number of researchers over the years. In 1990, Hwang et al. (1990) studied the rate of methane hydrate formation from melting ice discs based on the rate of gas consumption. A two stage process was observed which started at the gas-water interface. The first stage was rapid, and led to the formation of a hydrate film which completely covered the interface. The second stage was slower and limited by the mass transfer of methane or water through the hydrate film. This two stage process has since been confirmed by a large number of researchers with a variety of guest...
molecules for hydrate formation from both ice and water (Mori and Mochizuki 1996; Staykova, et al. 2003; Kuhs et al. 2006).

Hydrate formation is an exothermic process so historically authors have suggested that the initial hydrate formation rate can be limited by heat removal from the growing hydrate film (Uchida et al. 1999; Mori 2001; Uchida et al. 2002). However, it has also been shown that the film growth rate is also highly dependent on the solubility of the guest molecule in the water phase (Taylor et al. 2008); films formed from more soluble hydrate formers such as CO$_2$ grow much faster than from less soluble hydrate formers (Mochizuki and Mori 2006; Taylor et al. 2008). Heat transfer models for hydrate film growth, in which the film thickness is used as a fitting parameter, are unable to explain differences between the fitted film thickness for some results in the literature (Mori 2001; Mochizuki and Mori 2006). In addition, it has been shown that CO$_2$ hydrate forms a thicker initial film than methane hydrate at the same subcooling (Peng et al. 2008). This is opposite to the thicknesses regressed from the heat transfer models (Mochizuki and Mori 2006), indicating that mass transfer of the guest to the growing hydrate film is also an important factor in determining the growth rate of the film. A recent comparison of a mass transfer and a heat transfer model for hydrate film growth showed that mass transfer was much slower during hydrate film formation (Mochizuki and Mori 2008).

The morphology of a hydrate film is dependent on its formation conditions such as pre-saturation of the water phase and subcooling. For pre-saturated water, hydrate films tend to be coarser at higher subcoolings with dendrites extending from the film into either the host phase (Ohmura et al. 1999; Ohmura et al. 2000; Ohmura et al. 2004; Ohmura et al. 2005) or the guest phase (Servio and Englezos 2003; Zhong et al. 2008). For unsaturated water, an initially thick hydrate film can form at
low subcoolings which later partially dissolves into the water phase making the film appear smoother (Sugaya and Mori 1996; Ohmura et al. 1999); at higher subcoolings the film is initially thinner but grows over time suggesting a faster mass transfer rate across the film (Ohmura et al. 2000). The morphology of a hydrate film also depends on whether the system is flowing or stagnant: films formed under water flow are initially coarser and thicken faster once the flow is stopped (Kobayashi et al. 2001). Surface active additives in the water such as PVP and PVCap can also affect the hydrate film formation. PVP increases dendrite formation and reduces the film growth rate, whereas PVCap reduces the growth rate but does not affect the morphology (Sakaguchi et al. 2003).

Once the initial film has formed across the interface, the film thickens over time becoming increasingly mass transfer limited. Several conceptual pictures for the mass transfer mechanism across a hydrate film have been proposed. A review of the rival models for mass transfer across a CO₂ hydrate film is provided by Mori (1998). The models are divided into three groups: diffuse shell models, permeable solid plate models, and sedimented particle aggregation models. It is proposed that no single model can explain all possible hydrate formation scenarios and that the mass transfer mechanism may be system dependent.

As the hydrate film develops, depressions may form (Servio and Englezos 2003), secondary hydrate films may grow (Uchida et al. 1999; Zhong et al. 2008), and in the case of emulsified water droplets, stochastic growth has been observed inside the droplet long after formation of the initial hydrate film (Moudrakovski et al. 2004). Scanning Electron Microscopy has revealed that methane hydrate exists as a mesoporous structure. The pores range in size from 0.1 to 1 μm (Kuhs et al. 2004) and tend to fill over time, making the hydrate more dense (Stern et al. 2004; Stern et
This pore filling phenomenon was also observed on a larger scale in the confocal Raman spectroscopy studies that were described in Chapter 5. It is expected that this pore filling phenomenon would lead to an increased mass transfer resistance as the film ages.

In this chapter, high pressure Differential Scanning Calorimetry was applied to quantify the growth rate of hydrate films at a gas-water interface. The experimental apparatus and procedure are described in Section 6.2. The mathematical model that was used to deconvolute hydrate growth from dissolved methane from hydrate growth by mass transfer is described in Section 6.3. Comparisons of the model predictions to the experimental results are shown in Section 6.4. Finally, the conclusions from this chapter are listed in Section 7.4.

6.1 Previous Studies of the Mass Transfer Rate in Hydrate

A number of researchers have attempted to quantify the mass transfer rate across a hydrate film using a variety of different experimental and modeling techniques. One problem with many of the experimental and macroscopic modeling techniques is that the results are averaged over the entire sample volume so the often stochastic nature of hydrate formation can be overlooked (Moudrakovski et al. 2004).

Although there is some disagreement on whether the guest or the host molecule is the most mobile species in the hydrate, it is generally accepted that the mass transfer rate across a hydrate film is dependent on the hydrate former. The mass transfer rate in CO$_2$ hydrate is approximately an order of magnitude higher than in CH$_4$ hydrate at similar temperatures or driving forces. The apparent gas-water permeation coefficient at -1°C for CO$_2$ hydrate was found to be approximately $10^{-15}$ m$^2$/s (Staykova et al. 2003) compared to $10^{-17}$ to $10^{-16}$ m$^2$/s for methane hydrate
Similar values for CO$_2$ hydrate were also obtained by other researchers (Uchida et al. 2003; Henning et al. 2000; Wang et al. 2002; Takeya et al. 2000). If water is indeed the most mobile species in the hydrate, as suggested in Chapter 5, this would indicate that the mobility of the water is dependent on the composition of the hydrate.

Two Monte Carlo studies of the mass transfer of hydrate formers through a hydrate film have been reported. The first study suggested that the diffusivity of CO$_2$ in hydrate was much higher than that of water in hydrate. A diffusivity of CO$_2$ in hydrate of 10$^{-12}$ m$^2$/s at 0°C was obtained, compared to 10$^{-23}$ m$^2$/s for water in hydrate at -73°C (Demurov et al. 2002). However, it is important to note that the estimated diffusivity of CO$_2$ in hydrate from these Monte Carlo simulations was approximately two orders of magnitude higher than that obtained experimentally. In the second study, Kinetic Monte Carlo Equilibrium Path Sampling was employed to study the mass transfer rate in methane hydrate. This study also suggested that guest molecules diffuse faster than water molecules in sI hydrate. A diffusivity of 10$^{-16}$ m$^2$/s was obtained for methane in sI hydrate (Peters et al. 2008); this value was similar to experimental observations.

6.2 Experimental Procedure to Study the Hydrate Growth Rate with High Pressure DSC

In this study High Pressure Differential Scanning Calorimetry (HP-DSC) was applied to study mass transfer limitations to hydrate formation. A hydrate film was allowed to grow at a hydrocarbon-water interface and then held at a constant temperature for a pre-determined hold-time. The sample was then heated to dissociate the hydrate. The difference between the exotherm of hydrate formation and the en-
dotherm of hydrate dissociation corresponds to the amount of hydrate that formed between the initial film formation and the hydrate dissociation. By performing a series of similar experiments with different hold times, the mass of hydrate as a function of time could be derived. A summary of the experimental procedure is shown in Figure 6.1 and an example thermogram is shown in Figure 6.2. A description of the HP-DSC is provided in Section 4.1.

Since these experiments were conducted below the ice point, ice nucleation was also possible. Ice could be distinguished from hydrate by the magnitude of the formation exotherm and the dissociation temperature as described in Section 4.3. The experiments where ice had nucleated were omitted from this study since the ice might have affected the results.

There were two contributions to the mass of hydrate formed during the hold period: hydrate formation from dissolved methane, and mass transfer of the hydrate formers through the hydrate film. A schematic diagram illustrating the expected concentration profile of dissolved methane in the water phase as a function of time after the hydrate film formed is presented in Figure 6.3. By modeling the diffusion of dissolved methane to the hydrate and then subtracting its contribution to the measured hydrate growth rate, the mass transfer resistance of the hydrate film to hydrate formers could be isolated.

6.3 Modeling the Diffusion of Dissolved Methane to the Hydrate Film

The diffusivity of methane in water at 4°C is approximately $8.5 \times 10^{-10}$ m$^2$/s (Witherspoon and Bonoli 1969). The equilibrium methane concentrations in the aqueous phase with and without a hydrate phase were estimated using Multiflash with the Association Model (CPA-Infochem). The estimated concentrations are listed
1. Add Water and seal the cell
2. Pressurize with methane slowly
3. Hold for 3 hrs to allow for complete gas saturation

4. Record initial mass of hydrate from exotherm
5. Hold
6. Heat
7. Record final mass of shell from endotherm

Figure 6.1. A Schematic of the Experimental Procedure for the Film Growth Measurements

Figure 6.2. An Example Thermogram for a Film Growth Measurement
in Table 6.1. The CPA Association model in *Multiflash* was found to be a good match to available experimental data for methane solubility in water (Chapoy et al. 2004) as shown in Table 6.2.

In order to de-convolute the contribution to the film growth of dissolved methane from the mass transfer of water molecules or gas molecules across the hydrate film it is necessary to first model the methane diffusion in the free water phase. One-dimensional Fick's Law in rectilinear coordinates applies (Equation 6.1). Two solution procedures were applied: an analytical solution, and a numerical solution.

The term $C_A$ represents the concentration of methane and $D_A$ is the diffusivity of methane in water. The term $C_{A0}$ is the concentration of methane in the water phase which is in equilibrium with the vapor phase, $C_{Ai}$ is the concentration of methane in equilibrium with hydrate, $Film$ is the thickness of the hydrate film and $\delta$ is the thickness of the sample cell.
Table 6.1. Methane Concentrations in the Aqueous Phase as Estimated by *Multiflash*

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Methane Concentration in the Aqueous Phase at 150 bar (kg/m³) In the Presence of Hydrate</th>
<th>Methane Concentration in the Aqueous Phase at 150 bar (kg/m³) In the Absence of Hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5</td>
<td>0.67</td>
<td>4</td>
</tr>
<tr>
<td>-7</td>
<td>0.53</td>
<td>4.1</td>
</tr>
<tr>
<td>-10</td>
<td>0.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table 6.2. Methane Concentrations in the Aqueous Phase as Estimated by *Multiflash* (CPA Assoc.) and *CSMGem* Compared to Experimental Data (Chapoy et al. 2004)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Pressure (bar)</th>
<th>Experiment</th>
<th><em>Multiflash</em></th>
<th><em>CSMGem</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.96</td>
<td>9.73</td>
<td>3.99E-04</td>
<td>3.97E-04</td>
<td>3.88E-04</td>
</tr>
<tr>
<td>1.96</td>
<td>15.65</td>
<td>6.31E-04</td>
<td>6.26E-04</td>
<td>6.10E-04</td>
</tr>
<tr>
<td>1.96</td>
<td>23.23</td>
<td>9.01E-04</td>
<td>9.05E-04</td>
<td>8.80E-04</td>
</tr>
<tr>
<td>1.96</td>
<td>28.2</td>
<td>1.06E-03</td>
<td>1.08E-03</td>
<td>1.05E-03</td>
</tr>
<tr>
<td>9.98</td>
<td>10.39</td>
<td>3.29E-04</td>
<td>3.48E-04</td>
<td>3.34E-04</td>
</tr>
<tr>
<td>9.97</td>
<td>18.1</td>
<td>5.58E-04</td>
<td>5.91E-04</td>
<td>5.66E-04</td>
</tr>
<tr>
<td>9.98</td>
<td>27.56</td>
<td>7.72E-04</td>
<td>8.72E-04</td>
<td>8.33E-04</td>
</tr>
<tr>
<td>9.98</td>
<td>59.77</td>
<td>1.50E-03</td>
<td>1.70E-03</td>
<td>1.61E-03</td>
</tr>
<tr>
<td>25.01</td>
<td>9.77</td>
<td>2.38E-04</td>
<td>2.44E-04</td>
<td>2.30E-04</td>
</tr>
<tr>
<td>25.01</td>
<td>25.42</td>
<td>6.13E-04</td>
<td>6.07E-04</td>
<td>5.70E-04</td>
</tr>
<tr>
<td>25</td>
<td>59.22</td>
<td>1.24E-03</td>
<td>1.28E-03</td>
<td>1.20E-03</td>
</tr>
<tr>
<td>24.98</td>
<td>159.07</td>
<td>2.46E-03</td>
<td>2.64E-03</td>
<td>2.43E-03</td>
</tr>
<tr>
<td>39.96</td>
<td>10.25</td>
<td>2.04E-04</td>
<td>2.06E-04</td>
<td>1.93E-04</td>
</tr>
<tr>
<td>39.96</td>
<td>25.34</td>
<td>4.43E-04</td>
<td>4.91E-04</td>
<td>4.60E-04</td>
</tr>
<tr>
<td>39.96</td>
<td>77.98</td>
<td>1.31E-03</td>
<td>1.32E-03</td>
<td>1.23E-03</td>
</tr>
<tr>
<td>39.96</td>
<td>179.98</td>
<td>2.33E-03</td>
<td>2.42E-03</td>
<td>2.22E-03</td>
</tr>
</tbody>
</table>
\[
\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2}
\]  \hspace{1cm} (6.1)

Boundary Conditions:

\[ C_A = C_{Ai} \ ; \ x = Film \ ; \ t \geq 0 \]  \hspace{1cm} (6.2)

\[ \frac{\partial C_A}{\partial x} = 0 \ ; \ x = \delta \ ; \ t \geq 0 \]  \hspace{1cm} (6.3)

Initial Condition:

\[ C_A = C_{A0} \ ; \ Film < x \leq \delta \ ; \ t = 0 \]  \hspace{1cm} (6.4)

6.3.1 Analytical Solution.

The partial differential equation (PDE) in Equation 6.1 can be split into two ordinary differential equations (ODEs) using the product method; the ODEs can then be solved with a Fourier series (Kreyszig 1997). Since the closed boundary condition is problematic, it is convenient to solve the symmetrical problem twice the distance \(Film < x < 2\delta - Film\). Only half of the solution is utilized. Using the dimensionless variable \(C\), the revised initial conditions and boundary conditions are given in Equation 6.6 and 6.5 respectively.

\[ C = 0 \ ; \ X = 0,1 \ ; \ t \geq 0 \]  \hspace{1cm} (6.5)

\[ C = 1 \ ; \ 0 < X < 1 \ ; \ t = 0 \]  \hspace{1cm} (6.6)
Where:

\[ C = \frac{C_A - C_{Ai}}{C_{A0} - C_{Ai}} \quad (6.7) \]

\[ X = \frac{x - Film}{2(\delta - Film)} \quad (6.8) \]

The resulting ODEs from the product method are shown in Equation 6.9 and 6.10 where the term \( \zeta \) is a constant and \( Z \) and \( \theta \) are functions depending on only one variable. The solution of the PDE is provided by the Fourier series as shown in Equation 6.11. The details of this derivation are provided in Appendix C.

\[ \frac{d^2 Z}{dx^2} + \zeta^2 Z = 0 \quad (6.9) \]

\[ \frac{d\theta}{dt} + \frac{\zeta^2 \theta D_A}{4(\delta - Film)^2} = 0 \quad (6.10) \]

\[ \frac{C_A - C_{Ai}}{C_{A0} - C_{Ai}} = \sum_{n=1}^{\infty} 4e^{-\frac{(2n-1)^2 \pi^2 D_A t}{4(\delta - Film)^2}} \sin \left[ \frac{(2n-1)\pi(x - Film)}{2(\delta - Film)} \right] \quad (6.11) \]

### 6.3.2 Numerical Solution.

The numerical solution of the PDE was found using the forward difference method (von Rosenberg 1969). The PDE is expressed in standard explicit form in Equation 6.12. The closed boundary condition was imposed by equating the two grid points at the bottom of the cell as shown in Equation 6.13. The comparison of the analytical solutions for 1000 steps to the numerical solutions is shown in Figure 6.4. The agreement between both models is excellent. The Gibbs Phenomenon
Figure 6.4. Predicted Concentration Profile of Dissolved Methane as a Function of Time After Hydrate Film Formation (Thompson 1992) is evident in the analytical solution at 0 minutes.

\[ \frac{C_{t+\Delta t} - C_t}{\Delta t} = D_A \frac{C_{i+1} - 2C_i + C_{i-1}}{\Delta x^2} \]  \hspace{1cm} (6.12)

\[ C_{i_{end}} = C_{i_{end-1}} \hspace{0.5cm} \text{for} \hspace{0.5cm} t \geq 0 \]  \hspace{1cm} (6.13)
6.4 Results from the Film Growth Measurements

Before initiating experiments in the DSC it was necessary to pre-saturate the water phase with methane. The saturation was achieved by holding the pressurized DSC cell at 30°C for three hours in a methane atmosphere prior to cooling to the hydrate formation conditions. The saturation period was estimated using a similar approach as described for the hydrate formation step. Before the saturation procedure was implemented the mass of hydrate formed in the nucleation exotherm was stochastic. However, when the water had been pre-saturated the results were reproducible (Lachance et al. 2008). The mass of hydrate at the end of each experiment was found from the dissociation endotherm. In order to study the mass of hydrate as a function of time, a series of repeat experiments were performed for different hold-times.

The mass of methane that was incorporated into the hydrate film from the aqueous phase was predicted by integrating the mass transfer rate (Equation 6.14) over time at the hydrate-water boundary, as shown Equation 6.15. The concentration gradient in the $x$ direction was found by differentiating Equation 6.11. The details of these derivations are shown in Appendix D.

\[
\frac{dm}{dt} = D_A a \left| \frac{dC_A}{dx} \right|_{x=\text{Film}} \tag{6.14}
\]

\[
m = \int_0^t D_A a \frac{dC_A}{dx} \, d\varphi \tag{6.15}
\]

In these experiments the effect of several key variables on the mass of hydrate formed were investigated. The variables included the subcooling, the gas composition, and the addition of a liquid hydrocarbon layer. The results are plotted in terms of
the mass of hydrate formed as a function of time. The predicted mass of hydrate formed from dissolved methane is plotted on the same figures for comparison.

The results for hydrate formation at three different subcoolings are shown in Figure 6.5. In the case of the experimental series at -10°C, most of the hydrate formation could be attributed to methane that was initially dissolved in the water phase, little mass transfer appears to have occurred across the hydrate film in the timescale of these experiments. However, for the experimental series at -7°C and -5°C, the mass of hydrate formed was significantly higher than could be attributed to dissolved methane alone; the film was more permeable to hydrate formers in these cases and that allowed for further hydrate growth beyond the contribution of the dissolved methane.

The addition of a liquid hydrocarbon layer on top of the water layer was found to greatly reduce the amount of hydrate formation as shown in Figure 6.6, either as a result of the additional mass transfer resistance to gas molecules between the gas phase and the hydrate, or due to the formation of a less permeable hydrate film. In the experiments with a hydrocarbon layer, thehydrate growth could again be explained by methane dissolved in the water layer. The hydrate growth was similar for both pure alkane layers and crude oils indicating little effect of surface active crude oil components on the hydrate growth rate.

The higher mass of hydrate formed at the -7°C isotherm compared to the -10°C isotherm is in contrast to some previous work that shows increased hydrate growth with higher subcooling (Taylor, 2006). However, the trend between the -7°C isotherm and the -5°C isotherm is consistent with the observations by Taylor (2006) and suggests a maximum in the mass of the hydrate film as a function of subcooling. This maximum was also reported by Lachance (2008) for the -10°C and the -5°C
Figure 6.5. Mass of the Hydrate Film as a Function of Time For Three Different Temperatures with the Predicted Mass of Hydrate Formed from Dissolved Methane Alone
Figure 6.6. Mass of the Hydrate Film as a Function of Time when a Thin Layer of Hydrocarbon was Added to the System
isotherm and suggests a different hydrate film morphology as the subcooling of the system is increased from 22°C to 25°C.

In industrial scenarios, structure II hydrate is the prevalent hydrate structure. In addition, heavier hydrate guest molecules than methane are present which also may have an impact on the mass transfer rate across the hydrate shell and subsequently on the hydrate formation rate. In order to investigate these effects, a methane-ethane gas mixture (75 mol% methane, 25 mol% ethane) was used to form a hydrate film from bulk water at -10°C using the same formation procedure as in the methane experiments. The thermodynamically stable hydrate structure for two gases is different: for pure methane structure I is thermodynamically stable, for the methane-ethane gas mixture structure II is thermodynamically stable. However, it has repeatedly been shown (Murshed et al. 2008; Ohno et al. 2008) that meta-stable hydrate structures are possible for such gas mixtures. It is therefore necessary to identify which structure or structures are present in these experiments.

The dissociation temperature was significantly different for the two gas mixtures. The melting endotherm for the pure methane system occurred at 16.5°C compared to 22°C for the methane-ethane mixture. These temperatures were similar to the hydrate equilibrium temperatures for the gas mixtures that were predicted by CSMGem to be 16.3°C for structure I hydrate in the pure methane system and 21.3°C for structure II hydrate in the methane-ethane system. Only one dissociation peak was observed in each system, indicating that the hydrate film consisted of only one structure for each system. Although compelling, the different dissociation temperatures between the two gases did not confirm the hydrate structure since the equilibrium temperature for structure I hydrate formed from the same methane-ethane gas mixture was predicted to be 20°C which was also close to the measured endotherm at 22°C.
In some of the experiments, ice nucleation occurred some time after the hydrate film had formed. These experiments had been omitted due to the possibility of ice affecting the results. However, in the cases where ice had nucleated, the unconverted water in the system froze, and its mass could be determined on heating from the melting endotherm. Since the total mass of water in the experiment was known, and assuming that all of the water had converted to either ice or hydrate, the latent heat of the hydrate phase could be determined from the melting endotherm of the hydrate phase.

The latent heat of ice Ih is known to be 334 J/g so the mass of ice formed could be found by dividing the melting endotherm of the ice phase by the latent heat of ice. The mass of water in the hydrate phase could then be found from the difference in the mass of water added to the system and the mass of ice that had formed. This allowed the latent heat of hydrate formation to be estimated assuming that the hydrate was 84 wt% water as predicted by CSMGem.

The latent heat was found to be approximately 730 J/g, much closer to the structure II latent heat (640 J/g) than structure I (460 J/g) (Handa, 1986). Based on these two pieces of evidence, it is concluded that the hydrate film consisted of structure II hydrate. The results for hydrate films formed from the gas mixture are compared to the hydrate films formed from pure methane in Figure 6.7. The hydrate growth was found to be significantly lower for the gas mixture than for the pure gas regardless of whether the latent heat of dissociation for structure I or structure II was used.

The effective diffusivity of hydrate formers through the hydrate films was regressed to the experimental data by subtracting the mass of hydrate that formed from dissolved methane from the experimentally measured hydrate mass. For the
Figure 6.7. Mass of the Hydrate Film as a Function of Time for sI Hydrate Formed from Pure Methane and sII Formed from a Methane-Ethane Mixture
purposes of these calculations it was assumed, for the sake of argument, that methane is the mobile species in the hydrate film. Similar calculations could also be performed based on water as the mobile species. A quasi-steady state approximation was made for these calculations; accumulation of methane in the film was neglected, the thickening of the film and hydrate growth inside pores or fissures within the film was expected to be slow in comparison to the mass transport rate across the film. The one-dimensional steady state Ficks Law (Equation 6.1) therefore applied.

The mass of hydrate formed over time is the sum of the mass of hydrate formed from dissolved methane and the mass of hydrate formed from the mass transfer of the hydrate formers across the hydrate film. The effective diffusivity of methane across the film was unknown and was regressed to the experimental data using the least squares method (See Figure 6.8). The regressed effective diffusivity for the experiments at -5°C was \(7.6 \times 10^{-13}\) m\(^2\)/s; for the experiments at -10°C the effective diffusivity was \(3.4 \times 10^{-13}\) m\(^2\)/s. However, it is apparent that the experimental observations and the predicted hydrate growth rates show markedly different trends. At short timescales the predictions under-predict and at longer timescales the predictions over-predict the hydrate growth rate. It appears that the effective diffusivity is time dependent, dropping off over time as the film anneals. This result coincides with the pore filling observations presented in Figure 5.5. At long time scales, the diffusivity would approach the values calculated by other laboratories of \(1 \times 10^{-17}\) to \(1 \times 10^{-16}\) m\(^2\)/s for long term experiments on hydrate formation from ice (Staykova et al. 2003; Kuhs et al. 2006).

It may be possible to develop an expression to describe the evolution of the effective diffusivity in the hydrate films over time. However such a function would only be a fit to the experimental data with no physical basis. In addition, it is
Figure 6.8. Mass of the Hydrate Film as a Function of Time For Three Different Temperatures with the Predicted Mass of Hydrate Formed from Dissolved Methane And Diffusion Through the Hydrate Film

desirable to avoid introducing fitted parameters into the model wherever possible.

6.5 Conclusions

The key conclusions of Chapter 6 are as follows:

1. Less permeable hydrate films form in the presence of a liquid hydrocarbon layer.

2. The growth rate of hydrate was found to increase with sub-cooling until the temperature was reduced below approximately -7°C (22°C subcooling). At a temperature of -10°C, the growth rate was reduced.

3. The mass transfer resistance increases as hydrate films age due to pore filling.
Chapter 7

MODELING HYDRATE FORMATION IN INDUSTRIAL FLOWLOOPS, FLOW WHEELS AND STIRRED VESSELS

An important step towards the industrial validation of the mass and heat transfer model for hydrate formation that was described in Chapter 3 is to compare the model predictions to hydrate formation data from laboratory scale stirred vessels and industrial flowloops.

The model predictions are compared to hydrate formation data from laboratory scale stirred vessels in Section 7.1 and to industrial flowloop data in Section 7.2. The model is shown to provide a reasonable prediction of the hydrate formation rate in two flowloops for four crude oils and one model oils with three different gas compositions.

7.1 Comparing the Model Predictions with Existing Data from a High Pressure Stirred Vessel.

Hydrate formation from water-in-oil emulsions in a stirred high pressure vessel was studied by Turner et al. (2009) using a water in Conroe crude oil emulsion with a 35 vol% water cut. Turner et al. were able to predict the experimentally observed hydrate formation rate using a shrinking core model in which the limiting step for hydrate formation was assumed to be the mass transfer rate through the growing hydrate film. The shape of the curve was found to match the experimental observations to reasonable accuracy. The best fit for the effective diffusivity was similar in magnitude to than other values in the literature of $1 \times 10^{-17}$ to $1 \times 10^{-16}$ m$^2$/s (Kuhs
et al. (2006). The mixing rate of the high pressure vessel was low to avoid gas entrainment which would have adversely affected the particle size measurements that were being taken at the time. However, in some subsequent experiments, Boxall (2009) found that the hydrate formation rate in the high pressure vessel could be drastically increased if the make-up gas were introduced directly into the oil phase below the agitator. Boxall (2009) attributed this to the reduced mass transfer resistance between the gas phase and the surface of the growing hydrate particles which was not considered in the model of Turner et al. (2009).

By linking the CSMHyK subroutine to Excel, the hydrate formation data from the experiments of Turner et al. (2009) could be compared to the predictions from both the kinetic and transport models for hydrate formation. The predictions from the kinetic model for different values of the lumped parameter $u$ are shown in Figure 7.1. None of the values of the lumped parameter could match the shape of the experimental data which exhibits a much more rapid decrease in the conversion rate than would be expected by the reduction in surface area alone. The predictions from the transport model are in much better agreement with the experimental data as shown in Figures 7.2 to 7.5.

7.2 Comparing the Model Predictions with Industrial Flowloop Data

The methodology to simulate industrial flowloops with OLGA was initially developed by Yang (2004) in conjunction with SPTGroup and is described by Turner et al. (2005) and Boxall et al. (2008 b). Since an OLGA simulation requires both inlet and outlet nodes, dummy lines are needed which are isolated from the flowloop geometry using valves as shown in Figure 7.6. Simulations can be performed for constant pressure and constant volume experiments.Constant pressure can be simulated using
Figure 7.1. Comparisons of the Intrinsic Kinetics Model Predictions to the Autoclave Data from the First Experiment by Turner et al. (2009) 400 rpm, 4°C, 43 bar
Figure 7.2. Comparisons of the Transport Model Predictions to the Autoclave Data from the First Experiment by Turner et al. (2009) 400 rpm, 4°C, 43 bar
Figure 7.3. Comparisons of the Transport Model Predictions to the Autoclave Data from the Second Experiment by Turner et al. (2009) 400 rpm, 4°C, 49 bar
Figure 7.4. Comparisons of the Transport Model Predictions to the Autoclave Data from the Third Experiment by Turner et al. (2009) 500 rpm, 4°C, 43 bar
Figure 7.5. Comparisons of the Transport Model Predictions to the Autoclave Data from the Fourth Experiment by Turner et al. (2009) 500 rpm, 4°C, 49 bar
an additional line connecting the flowloop to a constant pressure node. In Figure 7.6, this line is labeled *Gas Accumulator*.

### 7.2.1 Experiments at the ExxonMobil Flowloop

The ExxonMobil flowloop is 10 cm in diameter, 94.5 m in length and has a volume of 696 liters. The maximum working pressure of the flowloop is 70 bar. Most of the flowloop is contained within a temperature controlled chamber with the exception of a short dip section 3.5 m in length in which a sight-glass and an FBRM particle size analyzer are installed. A second sight glass is installed upstream of the dip section. Temperature within the chamber is maintained using forced air convection. Good heat transfer to the flowloop is ensured by twelve finned sections of the flowloop against which the air in the room is circulated. Cooling rates of around 4°C/hr are typically achieved. The fluid in the flowloop is circulated by a sliding vane pump which was chosen to reduce the effect of the pump on the hydrate slurry. A mass flow
and density meter was added to the flowloop prior to the 2007 experiments.

Pressure in the flowloop can be maintained throughout the experiment using a gas accumulator with a volume of 454 liters. The gas accumulator is connected to the flowloop in two locations. The first connection is between the top of the accumulator and the flowloop upstream of the dipped section. The second connection links the bottom of the gas accumulator to the flowloop downstream of the pump. The two connections help to ensure good mixing between the gas in the loop and the accumulator. However, for high liquid loading experiments the first connection is usually isolated to prevent excessive liquid entrainment into the accumulator. A schematic of the flowloop is shown in Figure 7.7.

The experiments at the ExxonMobil flowloop were all performed using Conroe crude oil with a chemical composition as shown in Table 7.1. Conroe is a light crude oil with a stock-tank density of 0.820 g/cm³ (API gravity of 41°), a viscosity of 4 cP, and oil-water interfacial tension of 22.3 mN/m and an asphaltene and resin content of 0.31 and 4.89 wt% respectively (Lachance 2008). Experiments were performed with two gas compositions: pure methane gas (sI hydrate former), and 75 mol% methane, 25 mol% ethane (sII hydrate former).

At the start of the experiment, the flowloop was loaded by first adding the oil and water on a volumetric basis and then later adding the gas gravimetrically. The pump was then started and the fluids were allowed to gently equilibrate at 21°C for at least an hour before the chamber was cooled to initiate hydrate formation.

In the case of repeat experiments with the same loading, the loop was heated back to 21°C for 1 hour to dissociate the hydrate and remove any residual structuring of the water (Wilson et al. 2008).
Table 7.1. The Chemical Composition of Conroe Crude Oil

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>methane 0.008</td>
</tr>
<tr>
<td>C2</td>
<td>ethane 0.011</td>
</tr>
<tr>
<td>C3</td>
<td>propane 0.117</td>
</tr>
<tr>
<td>iC4</td>
<td>i-butane 0.126</td>
</tr>
<tr>
<td>nC4</td>
<td>n-butane 0.366</td>
</tr>
<tr>
<td>iC5</td>
<td>i-pentane 0.620</td>
</tr>
<tr>
<td>nC5</td>
<td>n-pentane 0.707</td>
</tr>
<tr>
<td>C6</td>
<td>hexanes 2.075</td>
</tr>
<tr>
<td>C7</td>
<td>heptanes 6.906</td>
</tr>
<tr>
<td>C8</td>
<td>octanes 13.546</td>
</tr>
<tr>
<td>C9</td>
<td>nonanes 10.423</td>
</tr>
<tr>
<td>C10</td>
<td>decanes 8.179</td>
</tr>
<tr>
<td>C11</td>
<td>undecanes 6.306</td>
</tr>
<tr>
<td>C12</td>
<td>dodecanes 6.100</td>
</tr>
<tr>
<td>C13</td>
<td>tridecanes 6.966</td>
</tr>
<tr>
<td>C14</td>
<td>tetradecanes 6.382</td>
</tr>
</tbody>
</table>
7.2.2 Experiments at the University of Tulsa Flowloop

The University of Tulsa flowloop is smaller flowloop than that at ExxonMobil: 7.4 cm in diameter and 60 meters in length. The maximum working pressure of the loop is 140 bar. Experiments can be conducted in either constant pressure or constant volume mode depending on whether the pressure controller is enabled. The fluids in the flowloop are circulated using a twin screw pump and the temperature is controlled by glycol cooling jackets. Cooling rates of $3^\circ C/hr$ and $22^\circ C/hr$ are typically used. The flowloop is fitted with four sight glasses. A schematic of the flowloop is shown in Figure 7.8.

The experiments at Tulsa were conducted using city gas, a typical composition of which is shown in Table 7.2. Since hydrates preferentially enclathrate heavier molecules such as propane (Sloan and Koh 2008), the composition of gas in the loop...
Figure 7.8. A Schematic of the Tulsa University Flowloop (Dellecase et al. 2008)
Table 7.2. The Chemical Composition of Tulsa City Gas

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>1.05</td>
</tr>
<tr>
<td>CO2</td>
<td>1.23</td>
</tr>
<tr>
<td>C1</td>
<td>94.84</td>
</tr>
<tr>
<td>C2</td>
<td>2.35</td>
</tr>
<tr>
<td>C3</td>
<td>0.38</td>
</tr>
<tr>
<td>iC4</td>
<td>0.02</td>
</tr>
<tr>
<td>nC4</td>
<td>0.06</td>
</tr>
<tr>
<td>iC5</td>
<td>0.01</td>
</tr>
<tr>
<td>nC5</td>
<td>0.02</td>
</tr>
<tr>
<td>C6</td>
<td>0.04</td>
</tr>
</tbody>
</table>

is dynamic, with the methane concentration increasing as more hydrate is formed. The hydrate equilibrium temperature will therefore decrease over the experiment as the heavier hydrate formers are depleted. Flowloop experiments were performed with a range of fluids from model oils such as dodecane, Citgo 19 and Citgo 220, to crude oils including Troika, Buttermilk and Caratanga.

Caratinga is a heavy crude oil with a stock-tak density of 0.914 g/cm$^3$ (API gravity of 23°), a viscosity of 220 cP, and oil-water interfacial tension of 23 mN/m and an asphaltene and resin content of 6.2 and 14.3 wt% respectively (Sjöblom et al. 2009). Buttermilk is a light-to-intermediate crude oil with a stock-tank density of 0.843 g/cm$^3$ (API gravity of 36°), and an asphaltene and resin content of 4.2 and 13.1 wt% respectively (Volk and Serica 2005). Troika is also an intermediate crude oil with an anomalously low interfacial tension of 6 mN/m. The stock-tank density of Troika is 0.869 g/cm$^3$ (API gravity of 31°), the viscosity is 20 cP and the asphaltene and resin content are 3.3 and 7.9 wt% respectively (Sjöblom et al. 2009).
7.3 Modeling and Analysis Methods

The fractional conversion of water to hydrate is frequently used as a basis for comparison between the experimental data and the predictions from the hydrate formation model. However, in the experiments the fractional conversion of water to hydrate must be calculated from the measured properties and this introduces uncertainties.

Previously, the conversion of water to hydrate was calculated based using a virial equation of state for the gas phase using a fixed value for the gas compressibility (Boxall et al. 2009). The volume of the gas phase was found for each point in the experiment by subtracting the volume of the oil, water and hydrate phases from the volume of the flowloop and adding on the volume of the gas accumulator which changes with time. The temperature of the gas phase was assumed to be equal to the temperature of the gas accumulator. This is a reasonable assumption for high liquid loadings but less realistic for low liquid loadings where much of the gas phase is contained within the flowloop, several degrees colder than the temperature of the accumulator.

Calculating the volume of the oil phase in the pressurized flowloop also introduces an uncertainty since the liquid density was predicted from the RKS equation of state using PVTSim or Multiflash. The mass of the oil phase was assumed to be conserved throughout the experiment.

In addition, the more recent experiments in the ExxonMobil flowloop used a methane-ethane gas mixture. Since the composition of the hydrate is different from the gas phase composition, the composition of the gas can change as hydrate forms, which in turn affects the hydrate equilibrium temperature and to a lesser extent, the solubilities and fluid densities.
An alternative technique to estimate the fractional conversion of water to hydrate in the flowloop is to adopt a fully compositional approach. In this technique, the composition and densities of the accumulator gas, flowloop gas, oil and water phases are calculated for each data point using a P-T flash in Multi flash using an RKS equation of state with hydrates excluded as an available phase. The change in the gas phase volume from one point to the next is used to calculate the moles of guest molecules that are enclathrated between these two points. The composition of the hydrate formed under these conditions is found from a P-T flash and the moles of enclathrated components are subtracted from the overall moles available ready for the next data point.

This approach negates the previous problems with compositional changes during hydrate formation and with temperature differences between the accumulator and flowloop. However the approach assumes that the water, gas and oil phases are well mixed which may not be the case, particularly in experiments at low pumping speeds or for systems with rapid hydrate formation rates. Another key difference is that the Multi flash predictions of the Conroe crude oil density under experimental conditions was 0.750 g/cm\(^3\) which was somewhat lower than the PVT Sim predictions that were used previously of 0.790 g/cm\(^3\). This led to a smaller gas volume inside of the loop compared to the previous approach and a lower estimate of the hydrate conversion.

Another advantage of a compositional approach to calculating the hydrate conversion is that the gas composition is able to change with time. This is particularly important for the sII hydrate formation experiments in the ExxonMobil flowloop in which a methane-ethane gas mixture (75 mol% methane, 25 mol% ethane) was used. Hydrate formed from this gas mixture concentrates ethane, leading to an increase in the methane concentration of the vapor phase as hydrate forms (See Figure 7.9).
Figure 7.9. A Plot Showing the Estimated Vapor Phase Concentration as a Function of Time in the ExxonMobil Flowloop for Conroe Crude Oil, 70% Liquid Loading, Pump Speed 900 rpm, Water Cut 37%

Neither approach is entirely accurate, however the two approaches estimate markedly different water conversions as shown in Figure 7.10. For the remainder of this chapter, the earlier approach for calculating the water conversion will be applied to ensure consistency between this work and the work performed previously. However, at this stage it is important for reader to note that experimentally determined water conversions from flowloop experiments are far from certain which is an inherent problem with larger apparatuses where multiple effects are occurring simultaneously and are more difficult to deconvolute.
Figure 7.10. A Comparison of the Estimated Water Conversions for the Same Experiment But Using Two Different Calculation Techniques: ExxonMobil Flowloop for Conroe Crude Oil, 70% Liquid Loading, Pump Speed 1400 rpm, Water Cut 50%
7.3.1 Results from the Flowloop Experiments

Hydrate nucleation is a stochastic process as discussed in Chapter 4. This stochastic behavior was observed in the flowloop however, the subcooling at which nucleation occurred was much lower than in the DSC experiments presented earlier. This difference is attributed to the larger volume of the flowloop, the increased shear, and the increased concentration of impurities which provide suitable heterogeneous nucleation sites. All of these factors increase the probability of a critical nucleus forming. A plot of the probability of hydrate nucleation versus subcooling for experiments in the ExxonMobil flowloop using the methane-ethane gas mixture is shown in Figure 7.11. Although there is limited data, the data is best fit with a Gaussian curve with a mean subcooling of 3.3°C and a standard deviation of 1.2°C.

The growth rate and transportability of the hydrate is dependent on a number of system properties. A summary of the results from experiments in the ExxonMobil flowloop is provided by Boxall et al. (2008 a). A similar summary for the Tulsa University flowloop experiments is provided by Dellecase et al. (2008). The most sensitive parameters in both flowloops are the water cut and the pump speed. Higher pump speeds lead to a slight increase in the fraction of water converted to hydrate, possibly due to the smaller droplet sizes that are created under higher shear rates. The transportability of hydrate slurries is improved as the pump speed is increased possibly due to the break up of aggregates under shear. Higher water cuts lead to a reduction in the transportability of the hydrate slurry and a reduction in the fraction of water that is converted to hydrate.

The ExxonMobil flowloop is fitted with two sight glasses and the Tulsa University flowloop with four. When the system was flowing, the water phase was observed to be fully entrained into the oil phase. As the system cooled and hydrate nucleated, small
Figure 7.11. The Probability of Hydrate Nucleation as a Function of Subcooling in the ExxonMobil Flowloop with the Methane-Ethane Gas Mixture
snow-like hydrate aggregates were observed. These aggregates remained dispersed throughout the hydrate formation step. However, upon heating, the hydrate became more gelatinous in nature, sticking and smearing across the sight glass. The bulk temperature of the fluid at this point was approximately $2^\circ C$ lower than the hydrate equilibrium temperature but the temperature of the temperature of the surroundings was above the hydrate equilibrium temperature. As the hydrate dissociated further, a free water phase was observed in the flowloop. The water phase persisted for several minutes until being re-entrained into the oil phase. A selection of images from the ExxonMobil experiments is shown in Figure 7.12.

The flowloop behavior is attributed to the water released from hydrate dissocia-
tion wetting the remaining hydrate particles and providing strong capillary attraction. As more water is released and the concentration of hydrate in the water decreases, the hydrate particles have less interaction and eventually form a separate water phase with dispersed hydrate particles. This conceptual picture is similar to that presented previously (Li and Hemmingsen 2009) in which a critical water cut is proposed that leads to maximum agglomeration. Additionally, the formation of the free water phase following hydrate dissociation is consistent with previous work by Greaves (2007) in a high pressure stirred vessel fitted with a Particle Video Microscope (PVM).

7.3.2 Results from the ExxonMobil Flowloop Experiments and Simulations

The CSMHyK-OLGA model predictions were compared to hydrate formation data collected from the ExxonMobil flowloop. The predictions were found to be in good agreement with the experimental data for two gas compositions using effective diffusivities that were in agreement with literature values (Kuhs et al. 2006).

Figure 7.13 shows the comparison of the simulation and experimental data for one of the flowloop tests that was performed with pure methane gas. Initially, the model overpredicted the hydrate formation rate, possibly due to the assumption of instantaneous nucleation of all of the water droplets. Later in the experiment, the model prediction agreed much better with the data. In contrast, the kinetics model with a fitted scaling factor of 0.002 provided a better match of the initial hydrate formation rate but diverged further into the experiment. The transport model also provided a reasonable prediction of the formation rate for structure II hydrate that was formed from a methane-ethane gas mixture. The predictions were in good agreement with the experimental data with literature values for the effective diffusivity
Experimental Data

- Kinetic Model $u=0.002$
- Transport Model $D=2\times10^{-17} \, \text{m}^2/\text{s}$

Figure 7.13. Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Conroe Crude Oil: 60% Liquid Loading, 100 mol% Methane, Pump Speed 280 rpm, 35 vol% Water cut and droplet sizes of 40 $\mu$m as shown in Figure 7.14 to 7.17.

7.3.3 Results from the Tulsa University Flowloop Experiments and Simulations

The model predictions were also found to agree with data collected from the Tulsa University flowloop for four different oils and for two different cooling rates using similar effective diffusivities than the ExxonMobil simulations. Comparisons of the model predictions to the flowloop data are shown in Figures 7.18 to 7.23.

It will be noted that the hydrate formation in the flowloop stopped abruptly
Figure 7.14. Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Conroe Crude Oil: 70% Liquid Loading, 75 mol% Methane 25 mol% Ethane, Pump Speed 900 rpm, 37 vol% Water cut, Cooled to 4°C
Figure 7.15. Comparisons of the CSMHyK-OLGA Predictions to ExxonMobil Flow Loop Data for Conroe Crude Oil: 70% Liquid Loading, 75 mol% Methane 25 mol% Ethane, Pump Speed 1400 rpm, 37 vol% Water Cut, Cooled to 4°C
Figure 7.16. Comparisons of the CSMHyK-OLGA Predictions to ExxonMobil Flow Loop Data for Conroe Crude Oil: 70% Liquid Loading, 75 mol% Methane 25 mol% Ethane, Pump Speed 900 rpm, 37 vol% Water Cut, Cooled to 10°C
Figure 7.17. Comparisons of the CSMHyK-OLGA Predictions to ExxonMobil Flow Loop Data for Conroe Crude Oil: 70% Liquid Loading, 75 mol% Methane 25 mol% Ethane, Pump Speed 1400 rpm, 37 vol% Water Cut, Cooled to 10°C.
Figure 7.18. Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Citgo 220 Model Oil: 50% Liquid Loading, Pump Speed 750 rpm, 25 vol% Water Cut, 2.8°C/hr

some time before the kinetic and transport model predictions. This is an artifact of the flowloop experiments since once the fluid becomes too difficult to pump it tends to slow down forcing the pump to run dry (Boxall, 2009). The stationary oil phase would introduce an additional resistance to mass transfer that is currently not considered in the \textit{CSMHyK - OLGA} model.

The transport model generally over-predicted the initially observed hydrate formation rate in both flowloops. This is contrary to the film growth results described in Chapter 6 in which the model under-predicted the initial hydrate formation rate. In the film growth measurements, only one hydrate film was formed in each experiment.
Figure 7.19. Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Buttermilk Crude Oil: 50% Liquid Loading, Pump Speed 750 rpm, 25 vol% Water Cut, 2.8°C/hr
Figure 7.20. Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Caratinga Crude Oil: 50% Liquid Loading, Pump Speed 750 rpm, 25 vol% Water Cut, 2.8°C/hr
Figure 7.21. Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Troika Crude Oil: 50% Liquid Loading, Pump Speed 750 rpm, 25 vol% Water Cut, 2.8°C/hr
Figure 7.22. Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Troika Crude Oil: 50% Liquid Loading, Pump Speed 750 rpm, 50 vol% Water Cut, 2.8°C/hr
Figure 7.23. Comparisons of the CSMHyK-OLGA Predictions to Flowloop Data for Troika Crude Oil: 50% Liquid Loading, Pump Speed 750 rpm, 25 vol% Water Cut, 22°C/hr
and these hydrate films were initially porous but annealed over time increasing the mass transfer resistance to hydrate formation. This led to an under-prediction of the initial hydrate formation rate. However, in the flowloops multiple droplets were present and not all droplets would nucleate simultaneously as the model assumed. The propagation of hydrate nucleation between droplets would slow the initially observed hydrate formation rate, leading to the model over-predicting the initial hydrate formation rate. The results shown in this chapter where the model over-predicted the initial hydrate formation rate suggest that the pore filling effect was negligible compared to the effect of nucleation propagation between droplets.

7.4 Conclusions

The key conclusions of Chapter 7 are as follows:

1. The hydrate formation rate in two industrial flowloops can be matched using the transport model for hydrate formation using literature values for the diffusivity of hydrate formers through a hydrate shell.

2. Water droplets and hydrate particles are fully dispersed in the oil phase in these hydrate formation experiments. Agglomeration was observed during hydrate dissociation.

3. The range of system pressures and cooling rates in the available flowloop data is limited which restricts the validation of the model.
Chapter 8

INDUSTRIAL APPLICATIONS

The transport model for hydrate formation that was described in Chapter 3 has a wide range of potential industrial applications from designing new facilities through to optimizing hydrate inhibitor injection rates for mature fields facing cost challenges. In this chapter, the model is applied to two hypothetical industrial case studies: a subsea tieback which served as the basis of a sensitivity analysis on the key parameters in the model (Section 8.1) and the simulation of the reaction zone in a stabilized flow system (Section 8.2).

8.1 Predicting Hydrate Plug Formation in a Subsea Tieback

The subsea tieback on which this sensitivity analysis is based was originally developed for evaluating the kinetics model (Boxall et al. 2008 b). A schematic of the tieback is shown in Figure 8.1 and an OLGA representation of the tieback is shown in Figure 8.2. The fluid was a typical crude oil with a stock-tank density of 0.824 g/cm$^3$ (API gravity of 40°). The water cut of the system was 35 vol%, and the Gas-to-Oil-Ratio (GOR) was 113 sm$^3$/m$^3$ at 15°C and 1 bar. Upon hydrate nucleation at 3.6°C (6.5°F) subcooling, the temperature of the system rose rapidly to the hydrate equilibrium temperature (See Figure 8.3) and further hydrate formation was limited by heat removal from the pipeline.

In order to better understand the most important parameters in the model, a sensitivity analysis was performed by adjusting one parameter at a time and studying
Figure 8.1. A Schematic Diagram of the Subsea Tieback to be Simulated (Boxall, 2009)
Figure 8.2. An OLGA Representation of the Subsea Tieback (Boxall, 2009)
Figure 8.3. A Profile Plot Showing Hydrate Formation Becoming Heat Transfer Limited
the change in the hydrate formation rate and the ratio of the slurry viscosity to
the crude oil viscosity. The parameters included in the analysis were: the effective
diffusivity, the nucleation criterion, the particle size scaling factor, the hydrate-oil slip
ratio, and the interparticle adhesion force.

The results of adjusting the effective diffusivity are shown in Figure 8.4. Three
effective diffusivities were considered: the base case (1×10^{-16} \text{ m}^2/\text{s}), an order of
magnitude higher (1×10^{-15} \text{ m}^2/\text{s}), and an order of magnitude lower (1×10^{-17} \text{ m}^2/\text{s}).
The result for the higher diffusivity simulation coincides almost exactly with the
base case simulation since the hydrate formation rate in both cases is limited by
heat removal from the pipeline. However, the slower diffusivity greatly reduces the
hydrate formation rate. In this simulation, the fluid temperature initially increases
rapidly back to the hydrate equilibrium line but then diverges away from the line
further down the pipeline indicating that the system becomes mass transfer limited
as the hydrate shells thicken. These results suggest that this particular system is
on the cusp of transition between a mass and a heat transfer limitation. In the
case of the flowloop simulations described in Chapter 7 the simulations were always
in a mass transfer limited regime due to the higher surface to volume ratio of the
smaller diameter pipeline which provided for more efficient heat transfer. In order to
accurately predict the hydrate formation rate in a wide range of industrial systems,
an understanding of both mass and heat transfer resistances will be critical.

The effect of increasing the nucleation criterion is to shift the onset of hydrate
formation further downstream (See Figure 8.5). In all cases, the hydrate formation
rate was initially rapid until the fluid temperature reached the equilibrium temper­
ature. After that the hydrate formation rate was similar in all systems since the
formation rate was limited by heat removal from the pipeline.
Figure 8.4. A Profile Plot Showing Effect of the Effective Diffusivity on the Hydrate Formation Rate
Figure 8.5. A Profile Plot Showing Effect of the Nucleation Criterion on the Hydrate Formation Rate
Figure 8.6. A Profile Plot Showing Effect of the Particle Size on the Hydrate Formation Rate

The size scaling factor is a pre-factor that is used to adjust the droplet size from the default of $40\mu m$. Adjusting this factor had two effects on the simulations: the smaller sized water droplets produced more hydrate as shown in Figure 8.6 due to the larger surface area available for hydrate formation. However, they also led to a larger increase in the slurry viscosity as shown in Figure 8.7. The higher viscosity was due to the larger effective volume of the hydrate aggregates for the smaller hydrate particles compared to the larger particles, since the aggregates of smaller particles occluded more fluid than the aggregates of larger particles for the same aggregate diameter.

The hydrate-oil slip factor $C_{OIL}$ had a profound effect on the volume fraction
Figure 8.7. A Profile Plot Showing Effect of the Droplet Size Scaling Factor on the Ratio of the Hydrate Slurry Viscosity Relative to the Oil
of hydrate present in the flow line and its distribution. Smaller slip factors caused hydrate to accumulate where it initially formed whereas higher slip factors allowed the hydrate to flow out of the flow line (See Figure 8.8).

The adhesion force in *CSMHyK version 2.0* is calculated from the subcooling of the system as described by Dieker (2009). Previously the adhesion force was fixed to 50 mN/m. However, the effect of manually fixing the adhesion force on the viscosity ratio of the hydrate slurry is shown in Figure 8.9. According to Dieker (2009), the interparticle adhesion force between dry cyclopentane hydrates is on the order of 5 mN/m. However, it has been shown that in some systems, particularly at low subcooling, large hydrate aggregates can be formed in the presence of unconverted
Figure 8.9. A Profile Plot Showing Effect of the Interparticle Adhesion Force on the Ratio of the Hydrate Slurry Viscosity Relative to the Oil

water (Li and Hemmingsen 2009) or from water droplet and hydrate particle collisions (Boxall 2009). The water droplet wets the hydrate particle before converting to hydrate. This mechanism has been shown for a THF hydrate particle contacting a water-THF droplet by Taylor (2006). The force between the droplet and the hydrate particle in this case are likely to be orders of magnitude higher than between dry hydrate particles. In Figure 8.9, little increase in the hydrate slurry viscosity occurs if the interparticle adhesion force from dry cyclopentane hydrate particles or from a capillary bridge is used. However, increasing the adhesion force by 1 to 2 orders of magnitude has a profound effect on the viscosity ratio.

As discussed in Section 3.3.3, CSMHyK version 2.0 is capable of tracking the
change in the dissolved salt concentration as hydrate forms, concentrating the salt in the remaining water. Figure 8.10 shows the results of a hydrate formation simulation in the subsea tieback when 4 wt% of salt has been added to the water phase at the wellhead. Upon hydrate nucleation, the fluid temperature rapidly increases to the hydrate equilibrium temperature as before. However, in this simulation the hydrate formation also causes an increase in the salt concentration of the water phase to 4.5 wt% which in turn causes a reduction in the hydrate equilibrium temperature. The effect is small in this simulation due to the small mass of hydrate formed compared to the mass of water available. In systems with lower water cuts, higher salt concentrations, or systems that are in the hydrate stability conditions for a longer period of time the effect of salt accumulation will be more pronounced.

8.2 Applying the Model to the CONWHYP Stabilized Flow Process

The transport model for hydrate formation was adapted to simulate the CONWHYP stabilized flow concept as described in Section 3.4. In the concept, water droplets from a wellstream are contacted with a fully converted subcooled hydrate slurry in the mixing zone. The warmer water droplets mix with the cold hydrate slurry at a temperature well below the hydrate formation temperature. The water droplets wet the hydrate particles thus increasing the surface area available for hydrate formation. The hydrate particles can then grow, rapidly consuming the water from the wellstream; this part of the process is called the reaction zone. In the industrial system, the hydrate slurry can then be split with part of the slurry being recycled back to the mixing zone, and the other part being transported to the processing facility (See Figure 3.7). Further downstream, other wellstreams can be introduced into the hydrate slurry flow line forming additional reaction zones.
Figure 8.10. A Profile Plot Showing the Effect of Salt Accumulation during Hydrate Formation
In developing an OLGA model of this process, the recycle loop shown in Figure 3.7 proved problematic. Firstly the hydrate slurry inside the recycle loop would need to be prepared prior to introducing the new fluid from the wellstream. The particle tracking scheme in OLGA meant that particles would need to be introduced prior to the formation of the hydrate slurry. Since there was no flow in the wellstream or flow line during this slurry formation step, the particles would diffuse into the wellstream and the flow line. Although the wellstream temperature was maintained well above the hydrate equilibrium temperature, the particle tracking scheme in OLGA does not account for hydrate particle dissociation and hence although any hydrate that diffused into the wellstream rapidly dissociated, the particle tracer was still present when the wellstream was initiated and this led to in-homogeneities in the particle distribution. Also, an additional particle source in the recycle loop was required to replace the number of particles lost to the flow line. Finally, any transients in the system in terms of particle distribution or salt distribution took a long time to dissipate.

It was therefore suggested (Li, 2008) to use a single-pass simulation for the stabilized flow system as shown in Figure 8.11. In the single pass system, the transient effects caused by the recycle line are avoided and the system reaches a steady state much faster. A particle source was added to the slurry line and the particle flow rate was chosen to give the desired particle diameter based on the water flow rate. The water in the slurry line was allowed to convert completely to hydrate before the mixing zone using a long slurry line with good heat transfer.

The fully converted slurry was then mixed with a small amount of the wellstream fluid in a ratio of 10:1. The wellstream contained a small amount of salt (1 wt%). The salt concentration in the reaction zone rapidly increased as the water converted
Figure 8.11. An OLGA Representation of a Single-Pass Version of the CONWHYP Stabilized Flow Process
Figure 8.12. The Predicted Hydrate Formation Rates in the OLGA Simulation from the Stabilized Flow Model Showing the Effect of Salt Accumulation on the Water Conversion to hydrate (See Figure 8.12). The hydrate formation rate predicted by the stabilized flow model was much faster than that predicted by the kinetics model as shown in Figure 8.13. The higher conversion rate is attributed to the larger surface area available for hydrate formation. In the stabilized flow model, all of the hydrate particles are coated with water and contribute to the surface area available for hydrate formation. In the kinetics model, the surface area available for hydrate formation decreases as water droplets convert to hydrate; in the reaction zone little water is present and this corresponds to a small surface area.

The slowest step in the hydrate formation is exported from CSMHyK – OLGA as an output variable. In the case of the stabilized flow simulations the slowest step
Figure 8.13. A Comparison of the Predicted Rate of Water Consumption due to Hydrate Formation for the Kinetics and Stabilized Flow Models
or limiting mechanism for hydrate formation was the rate of heat transfer from the particle as shown in Figure 8.14. This is to be expected since the mass transfer resistance of the thin water film (less than 1 \( \mu \text{m} \)) will be much less than that of the hydrate shell in the transport model.

The exothermic nature of hydrate formation raises the temperature of the fluid. At the same time, the salt exclusion leads to an increase in the salt concentration and a corresponding reduction in the hydrate equilibrium temperature. Further hydrate formation is limited by heat removal from the pipeline. Heat transfer from the pipeline is modeled in OLGA so is not reflected in the limiting mechanism shown in
Figure 8.14. The transition in the limiting mechanism for hydrate formation from heat removal from the individual particles to heat removal from the pipeline corresponds to a drop in the rate of water conversion; the last 0.05 μm of the water film in Figure 8.14 becomes increasingly difficult to convert to hydrate as the salt becomes more concentrated.

In the CONWHYP stabilized flow concept the hydrate formation rate should be high compared to the rate of particle collisions to avoid particle agglomeration in the reaction zone. In CSMHyK, there is as yet no dependence of the interparticle force on the fractional conversion of water to hydrate and the agglomeration is instantaneous leading to a steady-state agglomerate size as calculated from a force balance (Camargo and Palermo 2002).

For the cold flow model, it was decided to set the interparticle adhesion force to zero to avoid particle agglomeration in the simulations. The adhesion force was found to have little effect on the relative viscosity as shown in Figure 8.15; the results were similar for an adhesion force of zero and for an adhesion force of 50 mN/m, the maximum theoretical value from a capillary bridge.

The fluid used for these simulations was provided by StatoilHydro (Li, 2008) and is a typical North Sea crude oil with a water cut of 15 volume %, a stock tank density of 0.821 g/cm³ (API gravity = 40°) and a Gas-to-Oil-Ratio of 150 sm³/m³ at 15°C and 1 bar.

A sensitivity analysis was performed on the single-pass cold flow system focusing on four variables: the slurry particle diameter, the reaction zone pipe diameter, the wellstream temperature, and the slurry flow rate. Table 8.1 summarizes the simulation matrix for the sensitivity analysis.

The effect of changing the particle size of the hydrate slurry is shown in Fig-
Figure 8.15. A Comparison of the Predicted Hydrate Slurry Viscosities With and Without Particle Agglomeration

Table 8.1. The Simulation Matrix for the Sensitivity Analysis

<table>
<thead>
<tr>
<th>Input Parameters</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable</td>
<td>Base Case</td>
<td>Low</td>
</tr>
<tr>
<td>Droplet Diameter</td>
<td>40 mm</td>
<td>20 mm</td>
</tr>
<tr>
<td>Pipeline Diameter</td>
<td>20 cm</td>
<td>30 cm</td>
</tr>
<tr>
<td>Temperature of Wellstream</td>
<td>23.9°C</td>
<td>15.5°C</td>
</tr>
<tr>
<td>Slurry Flow Rate</td>
<td>90.7 kg/s</td>
<td>45.3 kg/s</td>
</tr>
</tbody>
</table>
Figure 8.16. The Effect of Particle Size on the Hydrate Formation Rate

The rate of hydrate formation in all three systems rapidly becomes limited by the rate of heat removal from the flow line but before this limit is reached, smaller particles convert the water to hydrate faster than larger particles due to the larger surface area and better heat transfer from the particles.

The diameter of the flow line used for the reaction zone has surprisingly little effect on the hydrate formation rate (See Figure 8.17). The smaller pipe diameter offers a larger surface to volume ratio but a shorter residence time than the larger diameter flow line. These two effects almost cancel each other out, the larger pipeline diameter leads to a slightly faster hydrate formation rate since the surface area of the pipeline per flow rate of slurry is higher (5/2 times), scaling with the pipe circumference.

The effect of the wellstream temperature on the hydrate formation rate was small
Figure 8.17. The Effect of Pipe Diameter on the Hydrate Formation Rate
Figure 8.18. The Effect of the Well Stream Fluid Temperature on the Hydrate Formation Rate

(See Figure 8.18). The slurry temperature was significantly lower than the hydrate formation temperature and since the flow rate of slurry was 10 times that of the wellstream, the sensible heat associated with the wellstream was small in comparison to the slurry.

Higher slurry to wellstream ratios led to faster hydrate formation rates (See Figures 8.19 to 8.21). One reason for this effect is the higher thermal mass of the slurry will allow for more hydrate formation before a heat transfer limitation is reached (See Figure 8.22). In addition, the surface area for hydrate formation will be larger if there are more slurry particles over which to divide the water.

One interesting point is that the intermediate flow rate initially reaches a higher
Figure 8.19. The Effect of the Slurry Flow Rate on the Hydrate Formation Rate for a 20 cm Diameter Pipeline
Figure 8.20. The Effect of the Slurry Flow Rate on the Hydrate Formation Rate for a 30 cm Diameter Pipeline
Figure 8.21. The Effect of the Slurry Flow Rate on the Hydrate Formation Rate for a 50 cm Diameter Pipeline
Figure 8.22. The Effect of the Slurry Flow Rate on the Fluid and Equilibrium Temperatures for a 30 cm Diameter Pipeline
conversion a shorter distance from the wellstream compared to the higher slurry flow rate. This is the case for all three pipe diameters (See Figures 8.19 to 8.21). This result is due to the slurry velocity increasing with the slurry flow rate leading to a shorter residence time.

8.3 Conclusions

The key conclusions of Chapter 8 are as follows:

1. The hydrate formation rate in industrial systems is close to a transition between mass transfer and heat transfer limited. Systems with low subcooling are more likely to be heat transfer limited, whereas systems with more hydrate present are likely to be mass transfer limited. An understanding of both is critical for accurate predictions.

2. The rate of hydrate formation in systems containing salt can rapidly decrease as salt accumulates.

3. The effective diffusivity and the size scaling factor have the greatest effect on the hydrate formation rate; the hydrate-oil slip factor has the greatest effect on the plugging potential of the system.

4. The hydrate formation rate predicted by the cold flow is higher than that of the kinetics model due to the larger surface area available for hydrate formation.
Chapter 9

HYDRATE PLUG DISSOCIATION

The formation of a hydrate plug in an oil or gas flow line has enormous implications for production, safety and cost. Hydrate plugs can take days or weeks to remediate and require significant infrastructure. The previous chapters in this thesis focused on predicting the rate of hydrate plug formation. This chapter will focus on how to remove a hydrate plug in the event that it forms. Section 9.1 of this chapter describes the current state of the art of hydrate plug remediation experiments and modeling. Section 9.2 describes a novel plug remediation technique which could be applied when the conventional techniques of inhibitor injection and depressurization are impractical. Section 9.3 describes extensions to the models for hydrate plug remediation in order to apply them to predict the rate of hydrate dissociation during the recovery of core samples in order to optimize recovery strategies.

9.1 Previous Studies of the Hydrate Plug Dissociation

Further understanding of the hydrate dissociation process and the ability to predict the dissociation rate are important for efficient hydrate plug remediation in flow lines, and for unlocking hydrates as an energy resource.

The hydrate plug remediation strategies can be divided into three broad categories (Lysne et al. 1995): pressure reduction, temperature increase and inhibitor injection. Several models have been proposed for hydrate plug remediation by pressure reduction on either one-side (Bollavaram, 2002) or on two sides (Jamaluddin et
Hydrate dissociation is an endothermic process so reducing the pressure of the hydrate plug below the hydrate equilibrium pressure would cause the hydrate phase to cool until the system reaches the new hydrate equilibrium temperature. In most cases, the hydrate equilibrium temperature for the depressurized pipeline would be well below the ice point so some or all of the water released from the dissociating hydrate plug could freeze forming a layer of ice around the dissociating hydrate plug. The ice would affect the hydrate plug dissociation in three ways:

1. The freezing of the water would release latent heat which would enhance the rate of hydrate dissociation.

2. The ice has a higher thermal diffusivity than water which would increase the heat transfer rate from the surroundings to the hydrate plug.

3. Ice may also be involved in the anomalously slow hydrate dissociation rate that occurs at temperatures just below 0°C. This anomaly has been observed by a number of researchers and is known as the self preservation effect (Stern et al. 2001). There is currently no broad agreement on the mechanism for the self preservation effect.

The models for hydrate plug dissociation by pressure reduction treat the process as being heat transfer limited, and apply Fourier's law of heat transfer in rectilinear (Kelkar et al. 1998) or cylindrical coordinates (Peters, 1999; Kofoed et al. 2002; Bollavaram, 2002) to model the moving boundary of the hydrate and ice phases as the plug dissociates. Since the rate of change of the temperature and size of the hydrate plug are slow soon after the pipeline has been depressurized, it has proven possible to apply a more computationally convenient quasi-steady state approximation to the
problem which reduces the computational complexity without adversely affecting the predictive capabilities (Kofoed et al. 2002).

The models for hydrate plug dissociation by two-sided depressurization are based on one-dimensional heat transfer in cylindrical coordinates. The system is assumed to be both radially and axially symmetrical with heat transfer from the pipeline wall to the hydrate plug through a fluid medium, typically assumed to be water. The temperature of the pipeline wall is typically fixed to ambient temperature but pipeline insulation can be accounted for by using a Biot number to scale the pipeline wall temperature between the ambient temperature and the temperature of the pipeline contents.

In the case of hydrate plug remediation by one-sided depressurization, there would be a pressure profile across the length of the hydrate plug. The pressure profile in the plug would depend on the system pressure upstream and downstream and on the effective permeability of the plug. The model for hydrate plug dissociation by one-sided depressurization (Bollavaram, 2002), divides the plug into sections and then calculates the position of the hydrate and ice boundaries for each section based on the local system pressure which is in turn calculated from Darcy’s law. Radial symmetry is again assumed in the one-sided depressurization model but the axial symmetry assumed in the two-sided depressurization model is relaxed. It is important to note that the one-sided depressurization model has had limited experimental validation due to the difficulties associated with producing and characterizing a low permeability hydrate plug in the laboratory.

The safest method of hydrate plug remediation is by depressurizing the plug evenly from both sides to below the equilibrium pressure at the seafloor temperature. This method avoids the formation of a pressure gradient across the plug,
which could cause it to detach from the pipeline wall and become a projectile with
enough momentum to cause severe equipment damage and loss of life. However, infre­
quently projectiles, can be created with two-sided depressurization, if multiple plugs
are present with pockets of pressurized gas trapped between them (Sloan, 2000).

In many industrial scenarios, access to one end of the plug is restricted and
it becomes impractical to depressurize a flow line from both sides and one-sided
depressurization must be used (Gjertsen et al. 1997; Xiao et al. 1998; Kashou et
al. 2004). In this case the hydrate plug dissociates on the downstream side, due
to the lower pressure, leading to a parabolic dissociation front. Once enough of the
downstream end of the plug has melted, it is possible that the pressure gradient across
the plug will be sufficient to detach the plug from the pipe wall, forming a projectile,
denser than the surrounding fluid. The consequences of this projectile depend on
the pressure gradient, the liquid content of the flow line, and the distance to any
processing equipment or radical flow line direction change.

In some deepwater field developments depressurization alone will be insufficient
to bring a plug out of the hydrate stability region due to the large residual head of
liquid present (Cochran, 2003). In these cases removal of the liquids is economically
prohibitive and heating the flow line wall to dissociate the hydrate plug may become
a more economically viable alternative.

Preventing hydrate plug formation during shut-in by heating the flow line, is an
established technology with many example applications (Geertsen and Offredi 2000;
Harrison and Herring 2000; Løken et al. 1999; Urdahl et al. 2003). The techniques
can be broadly divided into two categories: direct heating and indirect heating.

For indirect heating, the pipeline is heated by circulating a warm fluid through
a pipeline bundle (Harrison and Herring 2000), or by passing an electrical current
through heating elements which are wrapped around the pipeline (Geertsen and Of­
fredi 2000). In direct heating, electricity is conducted by the pipeline wall itself and
the impedance of the material causes the heating of the pipeline. Direct Electrical
Heating (DEH) has been installed by StatoilHydro and Shell on a number of subsea
flow lines (Urdahl et al. 2003; Luyties and Freckleton 2004) to keep the contents
above the hydrate formation temperature during shut-in. However, there is still some
debate on the risk of over-pressurizing of the pipeline if DEH were used to remediate a
hydrate plug due to the potential for trapping evolved gas from the dissociating plug.
In the case of the StatoilHydro operated Huldra field, the risk of over-pressurizing
the pipeline was considered too great to use DEH for plug remediation due to the
comparatively low flow line design pressure of 154 bar and the high heat flux required
(Urdahl et al. 2003). However, Shell have produced an annular flow model (Mehta A.
et al. 2001) that shows it can be safe to apply low, uniform levels of heat to remediate
a hydrate plug. The model demonstrates that for low heat fluxes, gas released during
dissociation would be able to escape through the annulus fast enough to prevent flow
line over-pressurization. These findings have not yet been experimentally verified.

9.2 Hydrate Plug Dissociation by Electrical Heating

The objective of this work was to investigate the dissociation rate of hydrate plugs
for two different hydrate structures at various pressures and with a variety of heat
input rates. A model was developed to describe the dissociation rate and this model
was incorporated into the CSM Plug hydrate remediation package to allow practicing
engineers to estimate dissociation times for industrial hydrate plugs treated by heat
input.

The effect of an oil phase on the dissociation rate was experimentally investigated
and the resulting dissociation rate was compared to the model prediction for a hydrate under the same conditions without an oil phase present. The pressure build-up from hydrate plugs dissociated in closed systems, with and without an oil phase present, were also investigated to verify the pressure increase calculated from an equation of state. This will provide the industry with a reliable method of estimating the maximum pressure that a pipeline could be exposed to if the gas released from a dissociating hydrate plug were contained by impermeable ends.

Finally, uneven heat input was investigated to simulate partial failure of an electrical heating system; heat was applied to one half of the cell and gas released from the other to maintain the cell pressure. The dissociation rate and pressures at either end of the hydrate plug were monitored to determine if pressure communication across the plug was maintained during the dissociation.

### 9.2.1 Electrical Heating Experimental Procedures

The hydrate plugs were generated in a 91.4 cm long stainless steel cell with a 2.54 cm internal diameter. The cell had been pressure tested to 210 bar. Five type T thermocouples were installed to measure the temperature at the center of the cell along the axial length. Transducers on either side of the cell were used to record the pressure during the hydrate formation and dissociation processes. The cell was connected to the pressure transducers via flexible hoses which allowed the cell to be removed from the bath without depressurizing the system. A back pressure regulator was installed to one side of the cell to maintain the pressure of the system as the hydrate plug dissociated. The rate of gas evolution from hydrate dissociation was measured with an inverted measuring cylinder that had been filled with water. A schematic of the experimental apparatus is shown in Figure 9.1.
The hydrates were prepared from powdered ice with a particle size range from 250-850 μm. The wall of the cell was cooled with liquid nitrogen before loading it with ice to reduce annealing of the particles. The mass of ice added was recorded to allow the final hydrate conversion and plug porosity to be calculated, assuming an even distribution of hydrate particles.

The cell was then sealed and placed in a temperature controlled glycol-water bath at (-2 ± 1°C) and then pressurized with the selected hydrate forming gas. The glycol water bath temperature was then increased to (0 ± 0.2°C) to allow free water to be produced from the melting ice which allowed the hydrate water lattice to form. Finely ground ice particles provide a large surface area for the gas to come into contact with, can provide an increased ability to absorb the enthalpy change released on hydrate formation (Hwang et al. 1990) and have residual hydrogen bonds in the free water from the ice quasi-liquid (Stern et al. 1996). This results in an increased hydrate formation rate.
The rate of pressure drop due to hydrate formation was observed to slow down rapidly before full conversion could be achieved. It was necessary to cool the bath to \((-2 \pm 1^\circ C)\) for a period of 1-2 hours and then increase it back to \((0 \pm 0.2^\circ C)\) in order to expedite the hydrate formation process. In previous work (Peters, 1999), this effect was attributed to an impermeable hydrate shell forming around the ice particles. By temporarily refreezing the free water, the expansion of the water core from the phase change produced fissures in the hydrate shell which permitted gas to diffuse to the free water surface. After 4-5 days the rate of pressure of the system had stabilized and the hydrate formation was deemed to be complete. The hydrate conversion at this point was estimated by considering the moles of gas consumed, calculated using the Peng Robinson Equation of State from the free gas volume and the pressure drop, and the mass of ice added at the start of the experiment. The calculation procedure is summarized in Appendix E. Hydrate conversions of 98 to 100 wt% were typical, based on the mass of ice added.

The hydrate plugs formed in these experiments were found to be highly permeable to gas which was important to ensure that evolved gas from the dissociating hydrate could escape without locally over pressurizing the system. Prior to dissociating the hydrate the pressure communication across the plug was tested by flowing gas through the hydrate plug and checking the pressure response on either side of the hydrate.

In order to dissociate the hydrate plug, the cell containing the hydrate was removed from the glycol-water bath and dried. Electrical heating pads mounted on the inside of a cylindrical copper sheath to reduce the effect of hotspots, were tightly clamped to the radial surface of the cell. The cell assembly was then wrapped in a 5 cm thick layer of ceramic insulation to reduce heat communication with the
surroundings. A variable resistor was used to set the heat input rate. Multi-meters recorded the RMS current being passed through, and the potential difference across the heating pads and hence the power input was calculated.

Eighteen experiments were conducted in total. Power inputs of 10, 20 and 30 W were investigated for both sI and sII natural gas hydrates at dissociation pressures of 70 bar and 140 bar. Structure I hydrates were made from pure methane; structure II hydrates were made from a methane-ethane mixture (65 mol% methane, 35 mol% ethane). The type of hydrate structure formed with this mixture at different pressures was predicted using CSMGem. When forming a sII hydrate, the cell pressure needed to be maintained above 16 bar during hydrate formation. This was to ensure that the sII hydrate was the thermodynamically stable structure rather than sI (Ballard and Sloan, 2001). For the sII experiments, the cell was initially pressurized to 140 bar and the hydrate was allowed to form until the pressure decreased to 100 ± 1.4 bar. The cell was then briefly depressurized to 14 bar for a short period prior to repressurization with the sII forming gas in order to fully replenish the ethane consumed in the formation. The structure of the hydrate formed using this method was verified by cooling the hydrate with liquid nitrogen and analyzing a sample using Raman spectroscopy (Hester, 2004). The Raman spectrum is shown in Figure 9.2. The peak positions observed were compared to published values for methane ethane sII hydrate (Subramanian, 2000).

9.2.2 Electrical Heating Model for Plug Remediation

A conceptual picture of the hydrate dissociation by electrical heating compared to two-sided and one-sided depressurization is presented in Figure 9.3. No ice phase is present when a hydrate plug is dissociated by heating since the hydrate equilibrium
The temperature of the pressurized system is generally above the ice point.

The limiting step in the dissociation is assumed to be the rate of heat transfer to the hydrate. This can be modeled using Fourier's Law of heat transfer in cylindrical coordinates (Equation 9.1). The initial conditions and boundary conditions are defined by Equation 9.2 and 9.3 to 9.5, respectively. The term $T_W$ in the equations is the water temperature, $T_H$ is the hydrate temperature, $\alpha_W$ is the thermal diffusivity of water, $k_W$ is the thermal conductivity of water, $Q_W$ is the heat transfer rate from the pipeline wall to the contents, $Q_H$ is the heat transfer rate to the hydrate plug, $r_p$ and $r_H$ are the pipeline and hydrate plug radii, respectively, $L$ is the length, $T_0$ is the initial temperature. The term $C_{PH}$ is the specific heat capacity of hydrate, $\rho_H$ is the hydrate density, $\lambda_H$ is the latent heat of hydrate dissociation, and $\epsilon$ is the porosity of...
Figure 9.3. A Comparison of the Conceptual Pictures for Hydrate Plug Dissociation
By: (a) Two-Sided Depressurization (Peters, 1999), (b) One-Sided Depressurization (Bollavaram, 2002), and (c) Electrical Heating
the hydrate plug.

Since many of these physical properties of industrial hydrate plugs are not known and the temperature of the hydrate plug is likely to remain close to the hydrate equilibrium temperature throughout the dissociation process, the temperature of the plug is assumed to be constant with respect to radius. Previous models for hydrate plug remediation by one- and two-sided depressurization (Peters, 1999; Bollavaram, 2002), used a boundary condition of constant pipe wall temperature. The radial electrical heating model described here uses a constant heat flux boundary condition.

Equations 9.1 to 9.5 are rewritten in terms of the dimensionless variables listed from 9.6 to 9.11. The dimensionless form of the Equations are displayed from 9.12 to 9.16. No analytical solution to the equation set was available so the equations were solved numerically by setting up a finite difference grid (Figure 9.4) and using the standard explicit scheme to calculate the water temperatures at the next time step. In standard explicit scheme the partial derivatives are rewritten as displayed in Equations 9.17 to 9.19. The time step in the finite difference grid must be small enough to prevent the solution from diverging (Incropera and DeWitt, 1996). A computer program was written using FORTRAN to compute the hydrate plug radius as a function of time, given the parameters listed in Table 9.1. No fitted parameters are used.

\[
\frac{\partial T_w}{\partial t} = \alpha_w \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T_w}{\partial r} \right) + \frac{\partial^2 T_w}{\partial r^2} \right] \tag{9.1}
\]

\[
T = T_H = T_0 \quad ; \quad 0 < r \leq r_p \quad ; \quad t = 0 \tag{9.2}
\]
\[ Q_W = -2\pi r k_W L \frac{\partial T_W}{\partial r} \mid r = r_p \mid t > 0 \quad (9.3) \]

\[ Q_H = -2\pi r k_W L \frac{\partial T_W}{\partial r} \mid r = r_H \mid t > 0 \quad (9.4) \]

\[ Q_H = -2\pi r L(1 - \epsilon) \rho_H \lambda_H \frac{\partial r_H}{\partial t} + \pi r_H^2 \rho_HC_P \frac{\partial T_H}{\partial t} \mid r = r_H \mid t > 0 \quad (9.5) \]

\[ R = 1 - \frac{r}{r_p} \quad (9.6) \]

\[ R_H = 1 - \frac{r_H}{r_p} \quad (9.7) \]

\[ t* = \frac{\alpha_W t}{r_p^2} \quad (9.8) \]

\[ Y = \frac{T_W - T_0}{T_D - T_0} \quad (9.9) \]

\[ V = \frac{T_D - T_H}{T_D - T_0} \quad (9.10) \]

\[ Q* = \frac{Q_H}{Q_W} \quad (9.11) \]

\[ \frac{\partial Y}{\partial t*} = \frac{-1}{1 - R \frac{\partial R}{\partial R}} + \frac{\partial^2 Y}{\partial R^2} \quad (9.12) \]
\[ Y = V = 0 \ ; \ 1 > R \geq 0 \ ; \ t^* = 0 \] (9.13)

\[ Q_W = 2\pi(1 - R)kWL(T_D - T_0)\frac{\partial Y}{\partial R} \ ; \ R = 0 \ ; \ t^* > 0 \] (9.14)

\[ Q_WQ^* = 2\pi(1 - R)kWL(T_D - T_0)\frac{\partial Y}{\partial R} \ ; \ R = R_H \ ; \ t^* > 0 \] (9.15)

\[ Q_WQ^* = \pi\rho_H\alpha_WL \left[ 2(1 - \epsilon)\lambda_H(1 - R_H)\frac{\partial R_H}{\partial t^*} - (1 - R_H)^2C_{PH}(T_D - T_0)\frac{\partial V}{\partial t^*} \right] \] (9.16)

\[ R = R_H \ ; \ t^* > 0 \]

\[ \frac{\partial Y}{\partial t^*} = \frac{Y_{i,j+1} - Y_{i,j}}{\Delta t^*} \] (9.17)

\[ \frac{\partial Y}{\partial R} = \frac{Y_{i+1,j} - Y_{i-1,j}}{2\Delta R} \] (9.18)

\[ \frac{\partial^2 Y}{\partial R^2} = \frac{Y_{i+1,j} - 2Y_{i,j} + Y_{i-1,j}}{\Delta R^2} \] (9.19)

\[ \frac{\partial R_H}{\partial t^*} = \frac{R_H|_{t^* + \Delta t^*} - R_H|_{t^*}}{\Delta t^*} \] (9.20)

\[ \frac{\partial V}{\partial t^*} = \frac{V_{i,j+1} - V_{i,j}}{\Delta t^*} \] (9.21)
Figure 9.4. The Finite Difference Grid that was Used to Numerically Simulate the Hydrate Plug Dissociation

Table 9.1. The Default Parameters Used in the CSMPlug Program for Industrial Hydrate Plug Dissociation by Electrical Heating

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Default Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation Temperature</td>
<td>12.2</td>
<td>°C</td>
</tr>
<tr>
<td>Ambient Temperature</td>
<td>4</td>
<td>°C</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Hydrate Structure</td>
<td>Structure II</td>
<td>-</td>
</tr>
</tbody>
</table>
9.2.3 Results from the Electrical Heating Experiments

The heat transfer model predicts the radial movement of the hydrate plug front as a function of time and this radial position as a function of time was used to predict the gas evolution rate. The predicted cumulative gas evolution rate is directly compared to the experimentally observed gas evolution in Table 9.2. The model predictions are in good agreement with the experimental observations. The predicted delay times for some of the experiments, prior to the dissociation commencing show discrepancies with the experimental observations. Specifically, the model predicts the dissociation will start earlier than is physically observed. This difference is attributed to the contribution of the cell wall that is not accounted for in the model; the cell wall must be heated from the water bath temperature (4°C) to the hydrate dissociation temperature which may be up to 16°C. The latent heat of dissociation is higher for sII hydrates than sI, hence sII hydrates have a longer dissociation time. The model predicts this difference in dissociation time to a good accuracy (See Figure 9.5).

Dissociation experiments were performed with a crude oil phase present to qualitatively observe its effect on the dissociation rate. The crude oil was injected into a preformed structure I hydrate plug by gas displacement. A low viscosity crude oil from the ExxonMobil Conroe field was chosen as the liquid phase, to facilitate the maximum possible filling of the hydrate pore spacing. The composition of Conroe is provided in Table 7.1.

Twenty Watts of heat were applied evenly to the radial surface of the hydrate plug and the free gas was released from the cell to maintain the pressure at 70 bar. The rate of gas evolved from the hydrate plug dissociating was compared to that of a hydrate plug dissociated under the same conditions without an oil phase present. The experimental results are presented in Figure 9.6. The pressure transducer readings
Table 9.2. A Comparison of the Experimental Results for Hydrate Plug Dissociation by Electrical Heating Compared to the Model Predictions

<table>
<thead>
<tr>
<th>Pressure</th>
<th>70 bar</th>
<th>140 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>Predicted</td>
<td>Observed</td>
</tr>
<tr>
<td>Structure I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 W</td>
<td>164</td>
<td>156</td>
</tr>
<tr>
<td>20 W</td>
<td>92</td>
<td>96</td>
</tr>
<tr>
<td>30 W</td>
<td>81</td>
<td>84</td>
</tr>
<tr>
<td>Structure II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 W</td>
<td>229</td>
<td>266</td>
</tr>
<tr>
<td>20 W</td>
<td>192</td>
<td>158</td>
</tr>
<tr>
<td>30 W</td>
<td>145</td>
<td>125</td>
</tr>
</tbody>
</table>

Figure 9.5. A Comparison of Electrical Heating Experiments and Model Predictions for sI and sII Hydrate
Figure 9.6. A Comparison of Electrical Heating Experiments With and Without Conroe Crude Oil

for at either end of the cell coincided throughout the experiment, even though the dissociated gas was only released from one side of the plug, indicating good pressure communication despite the presence of the oil phase. It can be seen from Figure 9.6 that the presence of the oil phase increased the dissociation time by approximately 10%. It is likely that this effect is attributable to the oil phase consuming some of the heat transferred from the pipe wall as the contents were heated.

An important consideration when dissociating a hydrate plug in the field is the maximum pressure accumulation that can occur if the gas evolved from the dissociating hydrate is contained by impermeable plugs at either end of the heated section of the plug. This pressure accumulation can be calculated by considering the volume of the plug, its porosity, the starting pressure and the relative volumes of gas and
water released by the plug dissociating. However, experimental verification is necessary before the predictions are acceptable to the Flow Assurance community at large. Two experiments were conducted in this work. The first experiment used a structure I methane hydrate plug with no oil phase present. This experiment served to give confidence in the theoretical calculations of the expected pressure increase, before the gas volume was reduced by addition of an oil phase in the second experiment. The cell was initially depressurized to 35 bar and then sealed. Twenty Watts of heat were applied evenly to the radial surface of the hydrate plugs in both experiments. The gas released by the dissociation was contained inside the cell. The gas pressure at either end of the cell was constantly monitored with pressure transducers. The results of the experiments are shown in Figure 9.7. It can be clearly seen that the addition of the oil phase significantly increased the rate of pressure build up in the system. With part of the pore space filled with oil, the pressure needed to be manually relieved three times to prevent it exceeding the cell test pressure of 210 bar. A total of 3000 cm$^3$ of gas was released. This corresponded to less than 10% of the total dissociated gas from the hydrate plug, suggesting the pressure would not have significantly exceeded 210 bar had the gas not been released.

Dissociation experiments were conducted on structure I hydrate plugs in which the heat flux was applied to only half of the cell. These experiments were designed to simulate the failure of a section of electrical heating material. Power inputs of 15 and 30 Watts were investigated. The heat flux was applied to the opposite end of the cell to which the gas was released. Figure 9.8 compares the dissociation rate of a hydrate plug dissociated with 30 Watts of heat applied to the radial surface of one half of the plug to the dissociation rate of a plug where the heat was applied evenly to the whole length. The dissociation rate was significantly reduced when uneven heating
Figure 9.7. A Comparison of the Pressure Increase During Electrical Heating Experiments in a Closed System With and Without Conroe Crude Oil
was applied as shown in Figure 9.8. This is attributed to the additional heat transfer resistance between the heated half of the plug and the un-heated half of the plug.

9.3 Predicting Hydrate Dissociation During Core Recovery

In 1965 it was recognized that natural gas hydrates were present in significant quantities in permafrost regions in the Soviet Union and had significant potential as an energy resource (Makogon, 1965). Today it is widely accepted that natural gas hydrates are present in oceanic sediments and permafrost regions at numerous locations around the world and contain more carbon than all other conventional fossil fuels combined. Estimates of the amount of hydrate bound gas contained in these deposits vary widely, but the most widely quoted estimates are in the range from
1\times 10^{14} \text{ to } 1\times 10^{15} \text{ m}^3 \text{ (Milkov, 2004).}

Core samples are frequently recovered from the ocean floor to verify the hydrate reserves and distributions inferred from seismic studies. Early studies relied on core barrels that were open to the ocean temperature and pressure profile as they were recovered. The two main examples of non-pressurized systems are the hydraulically driven Advanced Piston Corer (APC) (Ussler et al. 2002) and the rotated Extended Core Barrel (XCB) (Wallace et al. 2000). The latter is better suited to harder sediments. Core samples recovered by this method typically have a diameter of 5 cm and a length of 10 m. Cores recovered using either method exhibit extensive dissociation (Suess et al. 1988) which makes estimating the initial hydrates in place difficult. The rapid gas evolution has led to the extrusion of the sample from the core barrel during recovery (Pauli et al. 1996), and even rupture of the liner (Emeis et al. 1996; Dickens et al. 2003).

More recently pressurized coring tools such as the Pressure Core Sampler (PCS) (Dickens et al. 2003) or the Hyacinth Pressure Corer (Tréhu et al. 2004) have been used to reduce the dissociation of the core samples. The first successful deployment of a pressurized coring system was in 1995 on Blake Ridge (Seuss and von Huene 1988). The system used a ball valve to isolate the core from the surrounding ocean. This allowed the pressure produced from hydrate dissociating to be contained in the core thus reducing further dissociation as the core barrel was retrieved. Deployment of pressurized coring tools is time and resource intensive, and occasionally coring programs resort to un-pressurized coring systems (Dallimore et al. 2002). The ability to quickly estimate the percentage of hydrate dissociated by various methods will allow scientists to use available tools to make the most accurate assessment of hydrate deposits with limited resources and to modify the coring procedure to maximize the
percentage of the hydrate sample recovered.

The dissociation of hydrates has already been studied for two primary applications: to predict the productivity of hydrate reservoirs (Moridis, 2003), and to predict the dissociation rates of hydrate plugs inadvertently formed in oil and gas pipelines as discussed in Section 9.1. The aim of this work is to predict the dissociation rate of hydrate core samples recovered from the ocean floor. The model aims to exploit the geometrical similarities between core samples and pipeline plugs, so that the model development for hydrate plug dissociation can be applied to hydrate core recovery. The dissociation rate of hydrate plugs in pipelines was previously predicted with radial heat transfer models using a constant temperature (Peters, 1999; Bollavaram, 2002), or a constant heat flux boundary condition as described in Section 9.2.2. In the case of core recovery the thermal boundary condition will be transient and will depend on the temperature profile in the ocean with depth. This section describes how the heat transfer model for hydrate plug dissociation was adapted to predict the dissociation rate of hydrate core samples recovered from the ocean floor.

9.3.1 Experimental Setup and Procedures

Homogeneous cylindrical hydrate sediment cores were prepared and dissociated in the laboratory to validate the predicted dissociation rates from the heat transfer model.

The hydrate in sediment samples were generated in the same stainless steel cell as the electrical heating experiments (See Figure 9.1). The hydrates were prepared using a method developed by De Boer et al. (1985) from a mixture of de-ionized water and dry sand (US Silica F-110) with a particle size distribution of 100-250 μm. The water was mixed gravimetrically with the sand to provide the required
hydrate saturation. The cell was then sealed and placed in the temperature controlled glycol-water bath at 1°C and pressurized with the selected gas. The sample was re-pressurized as required, to replace the gas consumed by the hydrate formation. Conversions of water to hydrate of between 80 and 100% by mass were typically achieved. The structure I hydrate samples were formed from pure methane (Matheson Trigas 99.99% purity). Structure II hydrates were formed from a methane-ethane mixture (Matheson Trigas 75 mol% methane, 25 mol% ethane). Once the hydrate sample was formed, the water bath temperature was increased to 4°C to mimic typical seabed conditions. The system was allowed to equilibrate at this temperature for 2 hours prior to dissociation. The hydrate was then dissociated by increasing the bath temperature above the hydrate phase equilibrium temperature, by decreasing the pressure below the phase equilibrium pressure, or by a combination of the two.

Two pressure conditions were investigated: dissociation under constant pressure or dissociation in a closed system. The backpressure for the constant pressure experiments was set using a back pressure regulating valve. The hydrate dissociation rate was recorded by measuring the gas evolution from the hydrate during dissociation using an inverted graduated cylinder filled with water. In the case of dissociation in a closed system, the dissociation rate was calculated from the rate of increase of pressure, monitored using the pressure transducers, and converted to a gas evolution rate using the Peng Robinson equation of state.

The bath temperature was ramped to mimic the change in sea water temperature with depth as a core is recovered. The temperature profile achieved in the laboratory, compared well to that measured from an Advanced Piston Core (APC), during Leg 204 of the Ocean Drilling Program (ODP) at southern Hydrate Ridge near Oregon (See Figure 9.9).
Figure 9.9. A Comparison of the Temperature Ramp Achieved in the Laboratory Compared to that Experienced by a Core from ODP Leg 204 (Winters, 2005)
9.3.2 Modifications of the Model for Core Recovery

The limiting step in the dissociation was assumed to be the rate of heat transfer to the hydrate. This was modeled using Fourier's Law of heat transfer in cylindrical coordinates for the water, ice and hydrate layers. Only radial heat transfer was considered since the length of the core is much larger than the radius. It was assumed that the hydrate saturation in the sediment is initially homogeneous throughout the core, and that the free sediment released when the hydrate dissociates would keep the hydrated sediment at the center of the system as the hydrate dissociates. The system was assumed to be axially and radially symmetric, i.e. the free water produced from the dissociated hydrate would stay homogeneously dispersed and would not drain. In cases where the dissociation temperature of the sample is above the ice point (0°C), the system has a single moving boundary. In cases where the dissociation temperature of the hydrate is lower than 0°C, the free water produced from the dissociation process would freeze, forming an ice phase around the hydrate, the dissociation problem would then have a double moving boundary.

Three pressure conditions were modeled: constant pressure, open system and closed system. In the constant pressure condition, the system pressure remains constant throughout the core recovery process. In the open system, the pressure exerted on the hydrate core is a function of depth and decreases as the core is recovered. In the closed system, gas released from the dissociating hydrate accumulates inside the sample holder, increasing the pressure of the system as the core is recovered.

In all of the previous models for hydrate plug dissociation described in Section 9.1, the pressure of the system was fixed, thus fixing the hydrate dissociation temperature. However, in both the open and closed systems considered here, both the pressure and the dissociation temperature could fluctuate. In the case of the
open system, the pressure could be updated for each time step based on the depth, assuming a constant lifting rate.

The pressure for the closed system case must be calculated from the moles of free gas, the core temperature, and the free gas volume using the Peng Robinson equation of state. The free gas volume increases as the hydrate dissociates due to the higher density of water in liquid water or ice compared to hydrate. The equilibrium temperature of the hydrate was updated for each time step based on the new pressure using a fit to predicted hydrate equilibrium temperature for the gas composition as a function of pressure (See Figure 9.10). In addition to the pressure changes during recovery of the hydrate core, the temperature boundary condition will also change due to variations in the ocean temperature with depth (See Figure 9.9). In the model, the temperature profile with depth was accounted for by changing the boundary condition for each time step.

In the electrical heating model, only heat transfer in the water phase was considered since the constant pressure condition ensured a constant dissociation temperature of the hydrate plug. However, in the core recovery model the temperature profiles in all three phases are considered since both the ambient temperature and the hydrate equilibrium temperature are transient. A conceptual picture of the core dissociation is presented in Figure 9.11. The thermal properties of the composite phases were calculated from the pure component properties and their respective volume fractions. The pure phase properties used are shown in Table 9.3.

The finite element model described in Section 9.2.2 was used for the water, ice and hydrate phases. However, the previous definition of the dimensionless temperature shown in Equation 9.9 needed to be changed since the hydrate dissociation temperature is not constant in the core recovery experiments. The dimensionless
Figure 9.10. The Fits to the Predicted Hydrate Equilibrium Curves that were used in the Core Recovery Model

Figure 9.11. A Conceptual Picture of the Temperature Profile Inside a Dissociating Hydrate-In-Sediment Core Sample
Table 9.3. A List of the Thermal Properties of the Pure Phases that were used in the Model

<table>
<thead>
<tr>
<th>Phase</th>
<th>Heat Capacity (J/kg/K)</th>
<th>Density (kg/m³)</th>
<th>Thermal Conductivity (W/m/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>745</td>
<td>2650</td>
<td>6.5</td>
</tr>
<tr>
<td>Water</td>
<td>4200</td>
<td>1000</td>
<td>0.57</td>
</tr>
<tr>
<td>Methane</td>
<td>2518</td>
<td>29.5</td>
<td>0.034</td>
</tr>
<tr>
<td>Hydrate</td>
<td>2500</td>
<td>917</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Temperature for the core recovery model was defined with respect to the original hydrate dissociation temperature \(T_D\) as shown in Equation 9.22.

\[
Y = \frac{T - T_0}{T_D - T_0}
\]

(9.22)

The temperatures of the water, ice and hydrate phases were calculated from the standard explicit form of Equation 9.12. For the temperature of the grid points next to the moving boundaries, a three-point Lagrangian interpolation was used based on the temperature of the moving boundary and the temperatures of the two adjacent grid points as described by Peters (1999). A linear interpolation was used if the thickness of the phase was smaller than three grid points.

9.3.3 Results from the Core Recovery Experiments

The models developed in this work were verified by comparing the predicted results to a series of experiments. The experimental matrix is shown in Table 9.4. The hydrate sample porosities used in the model were calculated for each experiment using the initial mass of sand and water added to the cell and the volume of gas evolved during the experiment. The model predicted the position of the dissociating
Table 9.4. An Experimental Matrix for the Core Recovery Experiments

<table>
<thead>
<tr>
<th>Test</th>
<th>Temperature Condition</th>
<th>Pressure Condition</th>
<th>Saturation</th>
<th>Structure</th>
<th>Porosity</th>
<th>Particle Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Transient</td>
<td>Closed</td>
<td>45.9 %</td>
<td>I</td>
<td>0.5</td>
<td>100-250</td>
</tr>
<tr>
<td>2</td>
<td>Transient</td>
<td>Closed</td>
<td>51.1 %</td>
<td>I</td>
<td>0.5</td>
<td>100-250</td>
</tr>
<tr>
<td>3</td>
<td>Transient</td>
<td>Closed</td>
<td>45.4 %</td>
<td>II</td>
<td>0.5</td>
<td>100-250</td>
</tr>
</tbody>
</table>

front of the hydrate phase as a function of time for each experiment. This was used to calculate a corresponding gas evolution rate or the rate of pressure increase. The predicted dissociation rate was then compared to that observed experimentally.

Seven frequently applied models were used to estimate the thermal conductivities of the composite phases. The models are summarized by Huang and Fan (2005). The Arithmetic model sums the resistances in series and represents a lower bound, the Harmonic model sums the resistances in parallel and represents an upper bound. The geometric model represents random close packing. The other models used were the Krupiczka (1967), the Maxwell (1904), the Woodside Messmer (1961) and the Moridis (Moridis et al. 2005). The predicted composite thermal conductivities for the phase fractions used in Test 1 are shown in Figure 9.12.

The model predictions and experimental data for Tests 1 to 3 are displayed in Figures 9.13 to 9.15. The composite thermal conductivities of the hydrate, ice and dissociated sediment phases were varied between 1 and 3 W/m/K. A composite thermal conductivity of 2 W/m/K was found to best replicate the experiments in all cases. This thermal conductivity compared well to the various model predictions shown in Figure 9.12, but was significantly higher than the inverse modeling results of Gupta (2006) of 0.25-0.58 W/m/K, possibly due to the effect of water draining to
Figure 9.12. The Predicted Composite Thermal Conductivities for the Phase Fractions in Test 1
the bottom of the cell and increasing the heat transfer rate between the bath and the hydrate. The measurements by Gupta (2006) were taken half way up the cell so the problems of water draining could be avoided.

The experiments confirm that hydrate plugs with a diameter substantially less than the axial length will dissociate radially. However in real systems, the draining of the evolved water may increase the heat transfer rate at the bottom of the plug and increase the hydrate dissociation rate. It is likely that this draining effect partly explains the differences between the predicted and measured hydrate dissociation rates in these experiments.

The model predictions are sensitive to the core thermal conductivity, porosity
Figure 9.14. A Comparison of the Predicted and Measured Hydrate Dissociation Rates for Test 3
Figure 9.15. A Comparison of the Predicted and Measured Hydrate Dissociation Rates for Test 4
and hydrate saturation. In the field, these properties are rarely known. This limits the application of the model to an order of magnitude prediction of core dissociation. The hydrate is assumed to be homogeneously dispersed in the sediment and the effect on the thermal conductivity of free water draining is neglected. The models can be used to perform a sensitivity analysis on these key parameters in order to determine the best and worst case dissociation rates.

9.4 Conclusions

The key findings from Chapter 9 are as follows:

1. The dissociation rate of synthetic hydrate plugs by electrical heating can be predicted to a good accuracy by solving Fourier's Law in cylindrical coordinates with a moving boundary and a constant heat flux boundary condition.

2. Structure II hydrate plugs dissociate slower than structure I plugs due to their higher latent heat.

3. The experiments confirm that hydrate plugs with a diameter substantially less than the axial length will dissociate radially. However in real systems, the draining of the evolved water may increase the heat transfer rate at the bottom of the plug and increase the hydrate dissociation rate.

4. The heat transfer model for plug dissociation was applied to predict hydrate dissociation during the recovery of core samples.

5. The core recovery model is sensitive to the thermal conductivities, porosity and hydrate saturation of the sample which are rarely known in the field.
Chapter 10

SUMMARY OF CONCLUSIONS

The kinetic model for hydrate formation can be a useful tool for providing a worst-case prediction of the timescale for hydrate plug formation for gas dominated systems where the transport resistances to hydrate formation are small. However, accurate prediction of the location of the hydrate plug in flow lines will require improved predictions of water accumulation, hydrate wall growth, sloughing and jamming of hydrate deposits.

The predicted hydrate formation rate from the kinetic model is too high for oil dominated systems due to the additional heat and mass transfer resistances to hydrate formation. In the past, the transport resistances in industrial flowloops have been accounted for by using the temperature driving force and a lumped resistance parameter that was regressed to flowloop data. However, there was a question over how well this lumped parameter would transfer to the field.

In this work, a new transport model for hydrate formation was proposed that accounts for the mass and heat transport resistances to individual hydrate particles. The predicted growth rate in the new model agrees well with experimental data from two industrial flowloops using literature values for the diffusivity of hydrate formers through a hydrate shell. Sensitivity analyses on the new model revealed that the parameters that had the greatest effect on the predicted hydrate growth rate were the surface area and the effective diffusivity of the hydrate formers through the hydrate shell. The hydrate-oil slip factor had the greatest effect on the plugging potential of
the system. The hydrate formation rate in industrial systems was found to be close to a transition between mass transfer and heat transfer limited. An understanding of both is therefore essential for accurate predictions of the hydrate formation in all systems.

By linking the hydrate formation model to the *tracer tracking* module in *OLGA*, the effect of changing concentrations of thermodynamic inhibitors on the hydrate equilibrium temperature could be simulated. The rate of hydrate formation in such systems was shown to slow rapidly as salt accumulated. The model was also modified to simulate the *CONWHYP* stabilized flow process.

The development of the transport model was aided by laboratory-scale experimental studies. Visual techniques such as confocal Raman spectroscopy and non-visual techniques such as high pressure Differential Scanning Calorimetry were combined to provide qualitative and quantitative insight into the mechanisms of hydrate nucleation and growth.

It was found that although hydrate nucleation is a stochastic process, the probability of nucleation increases from almost zero to close to 100% within a narrow band of subcooling of a few degrees for both methane/water and xenon/water systems. This was demonstrated for experiments with a constant cooling rate and for isothermal experiments. In the constant cooling rate experiments, the cooling rate did not have a significant effect on the temperature of hydrate nucleation. In isothermal experiments, the time distribution of hydrate nucleation became narrower at higher subcoolings. Ice nucleation occurred within the same 2°C range, regardless of the pressure and cooling rate in the conditions investigated. In order to develop realistic probabilistic distributions for nucleation events in industrial systems, further experimental investigation is required in a wide variety of systems.
The mechanisms of hydrate film growth were elucidated using isotopic tracers. It was found that water molecules were more mobile than methane molecules within a methane hydrate film. This finding is important for correctly defining the driving force for hydrate formation in a mass transfer limited regime. The mass transfer resistance across a hydrate film was found to depend on the age of the film, the subcooling, and whether the film was formed in the presence of a hydrocarbon phase. As hydrate films age, the pores inside the film were observed to fill and the mass transfer resistance was found to increase. The hydrate films became more permeable as the subcooling was increased until the temperature was reduced below approximately -7°C (22°C subcooling). Finally, the hydrate films were found to be less permeable when they were formed in the presence of a liquid hydrocarbon layer.

If a hydrate plug forms in a deepwater flow line, it may be impractical to remove by depressurization alone due to the large liquid head. In such situations, dissociation by heating may become a viable alternative. The dissociation rate of synthetic hydrate plugs by electrical heating was predicted to a good accuracy by solving Fourier’s Law in cylindrical coordinates with a moving boundary and a constant heat flux boundary condition. Structure II hydrate plugs were found to dissociate slower than structure I plugs due to their higher latent heat. The experiments confirm that hydrate plugs with a diameter substantially less than the axial length will dissociate radially. However, in real systems, the draining of the evolved water may increase the heat transfer rate at the bottom of the plug and increase the hydrate dissociation rate. The heat transfer model for plug dissociation was adapted to predict hydrate dissociation during the recovery of core samples. The model was found to be sensitive to the thermal conductivities, porosity and hydrate saturation of the sample which are rarely known in the field.
It is suggested that any future work on the role of transport resistances in the formation or remediation of hydrate plugs should consider the following eleven recommendations that emerged as a result of this thesis:

1. Current models for hydrate plug formation are inadequate for gas dominated systems. The timescale for hydrate formation in a subsea gas tieback can be predicted to a reasonable accuracy using the intrinsic kinetic rate constant and zero slip condition, but the model cannot predict the correct location of the hydrate plug. Improved predictions are needed for water accumulation, hydrate wall growth, sloughing and jamming of hydrate deposits.

2. The transport model for hydrate plug formation in oil dominated systems was developed and tested for systems with a fully entrained water phase with minimal agglomeration. Less water entrainment would lead to two competing effects. The increased agglomeration of hydrate particles would lead to a smaller surface area for hydrate formation and a slower hydrate formation rate. However, increased agglomeration would increase the resistance of the slurry to flow and increase the risk of forming a hydrate plug. More research on the effect of a free water phase on hydrate particle agglomeration is needed.

3. The CONWHYP cold flow mechanism and model requires experimental validation and improvement before it can gain industrial acceptance for use in
design of industrial cold flow systems. In order to facilitate the further development of the model, it is suggested that industrial stakeholders such as BP and StatoilHydro continue to develop the model independently.

4. The nucleation studies that were described in this work provided some interesting insight into the physics behind the nucleation event. However, the subcoolings that were studied were too high to be industrially relevant. The larger volumes and the higher concentrations of nucleation sites that are provided by impurities mean that much lower subcoolings are needed for hydrate nucleation in industrial systems compared to the laboratory. A systematic study of the effect of common industrial impurities on the probability of hydrate nucleation would provide an indication of how well laboratory studies would transfer to the field.

5. All droplets in a pipeline section are assumed to nucleate simultaneously. At lower subcoolings this assumption may be invalid and it may be important to include a model for the nucleation propagation rate between droplets and a model for droplet-particle collisions.

6. The confocal Raman and Differential Scanning Calorimetry studies of the mass transfer mechanisms across a hydrate film that were described in this work were mainly limited to methane-water systems. Similar studies on CO$_2$-water and ethane-water systems would provide some useful insight into the effect of the hydrate former on the mass transfer mechanism. A study on a CO$_2$-water system would also be of interest for oceanic sequestration of CO$_2$ hydrate.

7. The industrial flowloop experiments that were modeled in this work were all performed for similar cooling rates and for constant flow rates. An important
extension of this work would be to study restart operations where water is allowed to separate and cool in dip sections before the flow is initiated. At ExxonMobil this type of experiment would need to be performed in the winter time.

8. In order to use the transport model for hydrate formation or the salt tracking model, lookup tables must be generated prior to the simulation. Integration of the CSMHyK module with compositional tracking in OLGA could potentially avoid the need for lookup tables.

9. In order to encourage widespread industrial acceptance and application of the CSMHyK – OLGA model, a simplified user interface, better documentation and more relevant industrial examples will be needed. Further consultation with SPTGroup and other relevant industrial partners will be required.

10. The studies of hydrate plug remediation by heating that were described in this work were conducted on highly permeable hydrate plugs in which the evolved gas could escape as the hydrate dissociated. These experiments were able to quantify the rate of hydrate plug dissociation, but were unable to offer insight into the risk of locally over-pressurizing the system if the hydrate plug were impermeable. Further studies are needed to assess the risk of over-pressurizing a flow line when applying heat to remediate an impermeable hydrate plug.

11. The core recovery experiments and model were developed for a horizontal configuration. In the field, cores are usually recovered vertically. The effect of water draining might have a significant effect on the dissociation rate of the hydrate core samples. Additional validation and improvement of the core recovery model is needed for a vertical geometry.
REFERENCES


Bermejo, D., Escribano, R., Orza, J.M., Absolute Raman Intensities of CH\textsubscript{4}, CH\textsubscript{3}D,


Blasius, H., Das Ähnlichkeitsgesetz bei Reibungsvorgängen in Flüssigkeiten, Forschungs-Arbeit des Ingenieur-Wesens, 1913. 131.


Christiansen, R.L., Bansal, V., Sloan, E.D., Avoiding Hydrates in the Petroleum In-


Creek, J.L., Personal Correspondence, 2006.


Demurov, A., Radhakrishnan, R., Trout, B.L., Computations of Diffusivities in Ice and CO₂ Clathrate Hydrates via Molecular Dynamics and Monte Carlo Simulations.


Goto, K., Hondoh, T., Higashi, A., Determination of Diffusion Coefficients of Self-


Hughes, T., Personal Correspondence, 2004.


Ikeda-Fukazawa, T., Horikawa, S., Hondoh, T., Molecular Dynamics Studies of Molecular Diffusion in Ice Ih. Journal of Chemical Physics, 2002. 117(8): 3886-3896.


Kobayashi, I., Ito, Y., Mori, Y.H., Microscopic Observations of Clathrate-Hydrate Films Formed at Liquid/Liquid Interfaces. I. Morphology of Hydrate Films. Chemi-


Li, X. Personal Correspondence, 2008.

Li, X., Hemmingsen, P.V. Plugging and Non-Plugging Hydrate Behavior in Diffennet


Maekawa, T., Experimental Study on Isotopic Fractionation in Water During Gas


Montesi, A. Personal Correspondence, 2005.


Moridis, G.J., Seol, Y., Kneafsey, T.J., Studies of Reaction Kinetics of Methane


Priestly, J., Experiments and Observations on Different Kinds of Air and Other Branches of Natural Philosophy Connected with the Subject (In Three Volumes). 1790. T. Pearson.


Sloan, E.D., Fleyfel, F., A Molecular Mechanism for Gas Hydrate Nucleation from


Strobel, T., Personal Correspondence, 2007

Strobel, T., Personal Correspondence, 2008


Winters, W. Personal Correspondence, 2006


Yang, S.O. Personal Correspondence, 2004

APPENDIX A

INPUTS AND OUTPUTS FOR CSMHYK FROM OLGA

The inputs and outputs for the hydrate formation model - CSMHyK - are listed in Tables A.1 to A.3. Table A.1 shows the inputs and outputs for the original kinetic model. Table A.2 shows the additional inputs and outputs that were added for the transport model. Finally, Table A.3 shows the inputs and outputs that were added for the tracer tracking model and for the cold flow model.
Table A.1. Original Inputs and Outputs for the Kinetic Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>I/O</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM</td>
<td>K</td>
<td>I</td>
<td>Operation temperature</td>
</tr>
<tr>
<td>PRS</td>
<td>Pa</td>
<td>I</td>
<td>Operation pressure</td>
</tr>
<tr>
<td>TEQ</td>
<td>K</td>
<td>I</td>
<td>Equilibrium temperature at system pressure</td>
</tr>
<tr>
<td>PEQ</td>
<td>Pa</td>
<td>I</td>
<td>Equilibrium pressure at system temperature</td>
</tr>
<tr>
<td>XK(2)</td>
<td></td>
<td>I</td>
<td>Multiplier for rate coefficients k1 and K2</td>
</tr>
<tr>
<td>XSIZE</td>
<td></td>
<td>I</td>
<td>Multiplier for particle monomer size</td>
</tr>
<tr>
<td>BEHYD</td>
<td></td>
<td>I</td>
<td>Volume fraction of hydrate in hydrate slurry</td>
</tr>
<tr>
<td>NP</td>
<td>N_p/m^3</td>
<td>O</td>
<td>Number of particles per unit volume</td>
</tr>
<tr>
<td>DA</td>
<td>m</td>
<td>O</td>
<td>Agglomerated particle size</td>
</tr>
<tr>
<td>VRATIO</td>
<td></td>
<td>O</td>
<td>Relative viscosity of hydrate slurry</td>
</tr>
<tr>
<td>NP</td>
<td></td>
<td>O</td>
<td>Number of particles per unit volume</td>
</tr>
<tr>
<td>DA</td>
<td></td>
<td>O</td>
<td>Agglomerated particle size</td>
</tr>
<tr>
<td>VRATIO</td>
<td></td>
<td>O</td>
<td>Relative viscosity of hydrate slurry</td>
</tr>
<tr>
<td>DP</td>
<td>m</td>
<td>O</td>
<td>Particle monomer size</td>
</tr>
<tr>
<td>GAS2H2O</td>
<td>kg/kg</td>
<td>O</td>
<td>Water consumed per gas consumed</td>
</tr>
<tr>
<td>GAS2HYD</td>
<td>kg/kg</td>
<td>O</td>
<td>Hydrate formed per gas consumed</td>
</tr>
<tr>
<td>SAREA</td>
<td>m^2/m</td>
<td>I</td>
<td>Surface area of water phase per meter of pipe</td>
</tr>
<tr>
<td>PSAREA</td>
<td>m^2/m</td>
<td>O</td>
<td>Surface area of particles per meter of pipe</td>
</tr>
<tr>
<td>VIS</td>
<td>Pa.s</td>
<td>I</td>
<td>Viscosity of hydrate carrying phase</td>
</tr>
<tr>
<td>DEN</td>
<td>kg/m^3</td>
<td>I</td>
<td>Density of hydrate carrying phase</td>
</tr>
<tr>
<td>GRATE</td>
<td>kg/s.m^2</td>
<td>O</td>
<td>Gas consumption rate from hydrate formation</td>
</tr>
<tr>
<td>GRATEDP</td>
<td>kg/sm^2/pa</td>
<td>O</td>
<td>Derivative of GRATE w.r.t. pressure</td>
</tr>
<tr>
<td>GRATEDT</td>
<td>Kg/sm^2/K</td>
<td>O</td>
<td>Derivative of GRATE w.r.t. temperature</td>
</tr>
<tr>
<td>ROHYD</td>
<td>kg/m^3</td>
<td>O</td>
<td>Hydrate density</td>
</tr>
<tr>
<td>CP</td>
<td>J/kgK</td>
<td>O</td>
<td>Heat capacity of hydrate</td>
</tr>
<tr>
<td>DELTAH</td>
<td>J/kg_{gas}</td>
<td>O</td>
<td>Enthalpy of hydrate formation</td>
</tr>
<tr>
<td>DELTAV</td>
<td>m^3/kg_{hydrate}</td>
<td>O</td>
<td>Volume change of hydrate formation</td>
</tr>
<tr>
<td>PLIST(1)</td>
<td>m^2/m</td>
<td>I</td>
<td>Oil and water interfacial area per pipe length</td>
</tr>
<tr>
<td>PLIST(2)</td>
<td>m^2/m</td>
<td>I</td>
<td>Gas in water interfacial area per pipe length</td>
</tr>
<tr>
<td>PLIST(3)</td>
<td>m^2/m</td>
<td>I</td>
<td>Water in oil interfacial area per pipe length</td>
</tr>
<tr>
<td>PLIST(4)</td>
<td>m^2/m</td>
<td>I</td>
<td>Oil in water interfacial area per pipe length</td>
</tr>
<tr>
<td>PLIST(5)</td>
<td>m^3/m</td>
<td>I</td>
<td>Volume of water per meter of pipe</td>
</tr>
<tr>
<td>PLIST(6)</td>
<td>s</td>
<td>I</td>
<td>Time since nucleation</td>
</tr>
<tr>
<td>PLIST(7)</td>
<td>s</td>
<td>I</td>
<td>Time step</td>
</tr>
<tr>
<td>PLIST(51)</td>
<td>m^2/m</td>
<td>O</td>
<td>Area for hydrate formation per pipe length</td>
</tr>
<tr>
<td>PLIST(52)</td>
<td>m</td>
<td>O</td>
<td>Average size of hydrate particle</td>
</tr>
<tr>
<td>PLIST(53)</td>
<td></td>
<td>O</td>
<td>Indicator for nucleation</td>
</tr>
</tbody>
</table>
Table A.2. Additional Input and Outputs for the Transport Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>I/O</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLIST(8)</td>
<td>K</td>
<td>I</td>
<td>Subcooling</td>
</tr>
<tr>
<td>PLIST(9)</td>
<td>W/m²/K</td>
<td>I</td>
<td>Thermal conductivity of aqueous phase</td>
</tr>
<tr>
<td>PLIST(10)</td>
<td>W/m²/K</td>
<td>I</td>
<td>Thermal conductivity of oil phase</td>
</tr>
<tr>
<td>PLIST(11)</td>
<td>J/kg/K</td>
<td>I</td>
<td>Specific heat capacity of aqueous phase</td>
</tr>
<tr>
<td>PLIST(12)</td>
<td>J/kg/K</td>
<td>I</td>
<td>Specific heat capacity of oil phase</td>
</tr>
<tr>
<td>PLIST(13)</td>
<td>kg/m³</td>
<td>I</td>
<td>Density of aqueous phase</td>
</tr>
<tr>
<td>PLIST(14)</td>
<td>kg/m³</td>
<td>I</td>
<td>Density of oil phase</td>
</tr>
<tr>
<td>PLIST(15)</td>
<td>m/s</td>
<td>I</td>
<td>Superficial velocity of aqueous phase</td>
</tr>
<tr>
<td>PLIST(16)</td>
<td>m/s</td>
<td>I</td>
<td>Superficial velocity of oil phase</td>
</tr>
<tr>
<td>PLIST(17)</td>
<td></td>
<td>I</td>
<td>Holdup of aqueous phase, fraction of pipe volume</td>
</tr>
<tr>
<td>PLIST(18)</td>
<td></td>
<td>I</td>
<td>Holdup of oil phase, fraction of pipe volume</td>
</tr>
<tr>
<td>PLIST(19)</td>
<td>Pa·s</td>
<td>I</td>
<td>Viscosity of aqueous phase</td>
</tr>
<tr>
<td>PLIST(20)</td>
<td>Pa·s</td>
<td>I</td>
<td>Viscosity of oil phase</td>
</tr>
<tr>
<td>PLIST(21)</td>
<td>m</td>
<td>I</td>
<td>Diameter of pipe</td>
</tr>
<tr>
<td>PLIST(32)</td>
<td></td>
<td></td>
<td>Limiting growth mechanism</td>
</tr>
<tr>
<td>PLIST(90)</td>
<td>m²/s</td>
<td>I</td>
<td>Diffusivity</td>
</tr>
<tr>
<td>PLIST(91)</td>
<td>m</td>
<td>I</td>
<td>Mean droplet diameter</td>
</tr>
<tr>
<td>PLIST(92)</td>
<td>N/m</td>
<td>I</td>
<td>Interfacial tension from OLGA</td>
</tr>
<tr>
<td>PLIST(93)</td>
<td></td>
<td>O</td>
<td>Subrange for the droplet calculations</td>
</tr>
<tr>
<td>PLIST(94)</td>
<td>m</td>
<td>O</td>
<td>Droplet diameter calculated by CSMHyK</td>
</tr>
<tr>
<td>PLIST(95)</td>
<td>m</td>
<td>O</td>
<td>Droplet diameter in the inertial subrange</td>
</tr>
<tr>
<td>PLIST(96)</td>
<td>m</td>
<td>O</td>
<td>Droplet diameter in the viscous subrange</td>
</tr>
<tr>
<td>PLIST(97)</td>
<td></td>
<td>O</td>
<td>Weber Number</td>
</tr>
<tr>
<td>PLIST(98)</td>
<td></td>
<td>O</td>
<td>Weber Star</td>
</tr>
<tr>
<td>PLIST(99)</td>
<td></td>
<td>O</td>
<td>Reynolds Number</td>
</tr>
<tr>
<td>PLIST(100)</td>
<td>N/m</td>
<td>O</td>
<td>Interparticle adhesion force</td>
</tr>
</tbody>
</table>
Table A.3. Additional Input and Outputs for the Tracer Tracking and Cold Flow Models

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>I/O</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLIST(22)</td>
<td>kg/kg</td>
<td>I</td>
<td>Mass fraction of MEG in water phase</td>
</tr>
<tr>
<td>PLIST(23)</td>
<td>kg/m³pipe</td>
<td>I</td>
<td>Mass of tracer nr. 1</td>
</tr>
<tr>
<td>PLIST(24)</td>
<td>s</td>
<td>I</td>
<td>Residence time of tracer nr. 1</td>
</tr>
<tr>
<td>PLIST(25)</td>
<td>s</td>
<td>I</td>
<td>Time of tracer nr. 1 subjected to subcooling</td>
</tr>
<tr>
<td>PLIST(26,27,28)</td>
<td></td>
<td>I</td>
<td>Repeat of 23, 24, 25 for tracer nr. 2</td>
</tr>
<tr>
<td>PLIST(29)</td>
<td>K</td>
<td>O</td>
<td>Hydrate equilibrium temperature with tracer</td>
</tr>
<tr>
<td>PLIST(30)</td>
<td>μm</td>
<td>O</td>
<td>Calculated hydrate particle diameter</td>
</tr>
<tr>
<td>PLIST(31)</td>
<td>wt%water</td>
<td>O</td>
<td>Calculated salt concentration</td>
</tr>
</tbody>
</table>
APPENDIX B

ACCOUNTING FOR DROPLET CURVATURE

A mass balance on a differential volume element of a sphere shown in Figure B.1 gives Equation B.1.

\[
\frac{dC}{dt} r^2 \sin \theta. d\phi. d\theta. dr = J_\phi r. dr. d\theta + J_\theta r. \sin \theta. d\theta. dr + J_r r^2 \sin \theta. d\phi. d\theta
\]  \hspace{1cm} (B.1)

Assuming no flux in the \( \phi \) or \( \theta \) direction, the mass balance reduces to Equation B.2

\[
\frac{dC}{dt} r^2 \sin \theta. d\phi. d\theta. dr = J_r r^2 \sin \theta. d\phi. d\theta
\]  \hspace{1cm} (B.2)

Assuming a quasi-steady state, i.e. neglecting mass accumulation, Equation B.2 becomes Equation B.3.

\[
0 = \frac{dC}{dt} r^2 = \frac{d}{dr} (J_r r^2)
\]  \hspace{1cm} (B.3)

Differentiating using the product rule gives Equation B.5.

\[
0 = \frac{d}{dr} \left( \frac{dC}{dr} r^2 \right)
\]  \hspace{1cm} (B.4)

\[
0 = \frac{2}{r} \frac{dC}{dr} + \frac{d^2C}{dr^2}
\]  \hspace{1cm} (B.5)
Figure B.1. Differential Volume Element on a Sphere from Bird et al. (2002)
Integrating using the substitution \( u = \frac{dC}{dr} \) gives Equation B.6. The constant \( A \) can be evaluated by applying the boundary conditions on the inside and outside of the hydrate shell: \( C = C_{in} \) at \( r = r_c \) and \( C = C_{out} \) at \( r = r_p \).

\[
\frac{dC}{dr} = Ae^{-2lnr} = \frac{A}{r^2} \tag{B.6}
\]

\[
\int_{C_{in}}^{C_{out}} dC = \int_{r_c}^{r_p} \frac{A}{r^2} dr \tag{B.7}
\]

\[
C_{out} - C_{in} = \frac{A}{r_c} - \frac{A}{r_p} \tag{B.8}
\]

\[
A = \frac{C_{out} - C_{in}}{\frac{1}{r_c} - \frac{1}{r_p}} \tag{B.9}
\]

Substituting the constant \( A \) into Equation B.6 gives Equation B.10.

\[
\frac{dC}{dr} = \frac{1}{r^2} \left[ \frac{C_{out} - C_{in}}{\frac{1}{r_c} - \frac{1}{r_p}} \right] \tag{B.10}
\]

At the surface of the hydrate particle, \( r = r_p \) and Equation B.10 becomes Equation B.11.

\[
\left. \frac{dC}{dr} \right|_{r=r_p} = \frac{r_c}{r_p} \left[ \frac{C_{out} - C_{in}}{r_p - r_c} \right] \tag{B.11}
\]

The analogous solution for the thermal gradient at the surface of the hydrate particle is given by Equation B.12.

\[
\left. \frac{dT}{dr} \right|_{r=r_p} = \frac{r_c}{r_p} \left[ \frac{T_{out} - T_{in}}{r_p - r_c} \right] \tag{B.12}
\]
APPENDIX C

FOURIER SOLUTION FOR THE DISSOLVED METHANE CONCENTRATION

The dissolved methane concentration profile in the DSC cell as a function of time is governed by Fick’s law (Equation C.1). Prior to the formation of the hydrate film, the water was presaturated with methane to a concentration of $C_{A0}$ by allowing equilibration with the gas phase. The corresponding initial condition of the system is therefore defined in Equation C.2. Upon formation of the hydrate film, the concentration of dissolved methane at the water-hydrate interface drops to the water-hydrate equilibrium concentration $C_{Ai}$. This boundary condition is described by Equation C.3. The bottom of the cell is closed to the concentration gradient at that point is zero, this is described by Equation C.4.

\[
\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \quad (C.1)
\]

\[
C_A = C_{A0} \; ; \; Film < x \leq \delta \; ; \; t = 0 \quad (C.2)
\]

\[
C_A = C_{Ai} \; ; \; x = Film \; ; \; t \geq 0 \quad (C.3)
\]

\[
\frac{\partial C_A}{\partial x} = 0 \; ; \; x = \delta \; ; \; t \geq 0 \quad (C.4)
\]
Equation C.1 and the initial and boundary conditions C.2 to C.4 can be written in terms of the dimensionless variables \( C \) (Equation C.5) and \( X \) (Equation C.6). The revised equations are shown in Equations C.12 to C.14. Since the closed boundary condition is problematic, it is convenient to solve the symmetrical problem twice the distance \((Film < x < 2\delta - Film)\). Only half of the solution is utilized.

\[
C = \frac{C_A - C_{Ai}}{C_{A0} - C_{Ai}} \quad \text{(C.5)}
\]

\[
X = \frac{x - Film}{2(\delta - Film)} \quad \text{(C.6)}
\]

\[
\frac{\partial C_A}{\partial t} = (C_{A0} - C_{Ai}) \frac{\partial C}{\partial t} \quad \text{(C.7)}
\]

\[
\frac{\partial^2 C_A}{\partial x^2} = (C_{A0} - C_{Ai}) \frac{\partial^2 C}{\partial x^2} \quad \text{(C.8)}
\]

\[
X = \frac{x - Film}{2(\delta - Film)} \quad \text{(C.9)}
\]

\[
\frac{dX}{dx} = \frac{1}{2(\delta - Film)} \quad \text{(C.10)}
\]

\[
\frac{\partial^2 C_A}{\partial x^2} = \frac{(C_{A0} - C_{Ai})}{4(\delta - Film)^2} \frac{\partial^2 C}{\partial X^2} \quad \text{(C.11)}
\]

\[
\frac{\partial C}{\partial t} = \frac{D_A}{4(\delta - Film)^2} \frac{\partial^2 C}{\partial X^2} \quad \text{(C.12)}
\]
The partial differential equation (PDE) in Equation C.12 can be split into two ordinary differential equations (ODEs) using the product method (Kreyszig 1997). First, the variable $C(X, t)$ is split into a product of $Z(X)$ and $\theta(t)$ which each depend on only one variable (See Equation C.15). By substituting the resulting partial derivatives C.16 and C.17 into Equation C.12, the PDE can be separated into a component dependent on $X$ only and a component dependent on $t$ only (See Equation C.18). Thus the PDE can be separated into two ODEs as shown in Equation C.19 where the term $\zeta$ is a constant. The sign of the ODEs must be negative to ensure a periodic solution. The ODEs (Equation C.20 and C.21) can be solved with a Fourier series (Kreyszig 1997).

\[ C = 0 \ ; \ X = 0, 1 \ ; \ t \geq 0 \]  \hspace{1cm} (C.13)

\[ C = 1 \ ; \ 0 < X < 1 \ ; \ t = 0 \]  \hspace{1cm} (C.14)

\[ C = Z(X) \theta(t) \]  \hspace{1cm} (C.15)

\[ \frac{\partial^2 C}{\partial X^2} = \frac{\theta \partial^2 Z}{\partial Z^2} \]  \hspace{1cm} (C.16)

\[ \frac{\partial C}{\partial t} = Z \frac{\partial \theta}{\partial t} \]  \hspace{1cm} (C.17)

\[ Z \frac{\partial \theta}{\partial t} = \frac{D_A}{4(\delta - Film)^2} \frac{\partial^2 Z}{\partial X^2} \]  \hspace{1cm} (C.18)
Equation C.20 is a Sturm-Liouville equation and can be expanded as a Fourier series as shown in Equation C.22. In order to satisfy the boundary conditions for $C$ shown in Equation C.13, $Z(0) = 0$ and $Z(1) = 0$, the coefficients $a_0$ and $a_n$ must be equal to zero. The resulting expression for $Z_n(X)$ can be differentiated twice with respect to $X$ and substituted into Equation C.20 to give Equation C.26.

\[
Z(X) = a_0 + \sum_{n=1}^{\infty} a_n \cos \frac{n\pi X}{L} + b_n \sin \frac{n\pi X}{L} \quad (C.22)
\]

\[
Z_n(X) = b_n \sin n\pi X \quad ; \quad n = 1, 2, 3, 4... \quad (C.23)
\]

\[
Z'_n(X) = b_n n\pi \cos n\pi X \quad ; \quad n = 1, 2, 3, 4... \quad (C.24)
\]

\[
Z''_n(X) = -b_n [n\pi]^2 \sin n\pi X \quad ; \quad n = 1, 2, 3, 4... \quad (C.25)
\]

\[-b_n (n\pi)^2 \sin n\pi X + \zeta^2 b_n \sin n\pi X = 0 \quad ; \quad n = 1, 2, 3, 4... \quad (C.26)\]
The second ODE (Equation C.21) can be solved by separation of variables to give Equation C.31. Substituting Equations C.31 and C.23 into Equation C.15, the dimensionless concentration profile can be expressed by Equation C.32.

\[ \frac{d\theta}{dt} = -\frac{\zeta^2 \theta D_A}{4(\delta - \text{Film})^2} \]  

\[ \theta = A e^{-\frac{\zeta^2 D_A t}{4(\delta - \text{Film})^2}} \]  

\[ \theta_n = A e^{-\frac{n^2 \pi^2 D_A t}{4(\delta - \text{Film})^2}} ; \quad n = 1, 2, 3, 4... \]  

\[ C = \sum_{n=1}^{\infty} A_n \sin n\pi X e^{-\frac{n^2 \pi^2 D_A t}{4(\delta - \text{Film})^2}} \]  

By applying the initial conditions given in Equation C.14: \( C = 1 \) at \( t = 0 \), Equation C.32 reduces to Equation C.33. The coefficient \( A_n \) is therefore evaluated from the Fourier sine series of the initial conditions as shown in Equation C.34 to C.35. Since \( n \) is an integer the value of \( \cos n\pi \) is either 1 or -1. Hence, \( A_n \) can be simplified to Equation C.36. Substituting Equation C.39 into Equation C.32 gives Equation C.40.
\[ A_n = 2 \int_0^1 \sin(n\pi X) \, dx \quad ; \quad n = 1, 2, 3, 4... \quad \text{(C.34)} \]

\[ A_n = \frac{2}{n\pi} (1 - \cos n\pi) \quad ; \quad n = 1, 2, 3, 4... \quad \text{(C.35)} \]

\[ A_n = 2 \frac{1 - (-1)^n}{n\pi} \quad \text{(C.36)} \]

\[ A_n = 0 \quad ; \quad n = 2, 4, 6, 8... \quad \text{(C.37)} \]

\[ A_n = \frac{4}{n\pi} \quad ; \quad n = 1, 3, 5, 7... \quad \text{(C.38)} \]

\[ A_n = \frac{4}{(2n-1)\pi} \quad ; \quad n = 1, 2, 3, 4... \quad \text{(C.39)} \]

\[ C = \sum_{n=1}^{\infty} \frac{4}{(2n-1)\pi} \sin((2n-1)\pi X) e^{-\frac{(2n-1)^2\pi^2 D_A t}{4(\delta - Film)^2}} \quad \text{(C.40)} \]

\[ \frac{C_A - C_{Ai}}{C_{A0} - C_{Ai}} = \sum_{n=1}^{\infty} \frac{4e^{-\frac{(2n-1)^2\pi^2 D_A t}{4(\delta - Film)^2}}}{\pi(2n-1)} \sin(\frac{(2n-1)\pi(x - Film)}{2(\delta - Film)}) \quad \text{(C.41)} \]
APPENDIX D

DETERMINING THE MASS OF HYDRATE FORMED FROM DISSOLVED METHANE

Equation 6.11 can be rearranged in terms of $C_A$ as shown in Equation D.1. The concentration gradient at the edge of the hydrate film ($x = \text{Film}$) is found by differentiating Equation D.1 and evaluating $x$ as shown in Equation D.3.

$$C_A = C_{Ai} + (C_{A0} - C_{Ai}) \sum_{n=1}^{\infty} \frac{4e^{\frac{(2n-1)\pi^2DAt}{4(\delta-\text{Film})^2}}}{\pi(2n-1)} \sin \frac{(2n-1)\pi(x - \text{Film})}{2(\delta - \text{Film})}$$  \hspace{1cm} (D.1)

$$\frac{dC_A}{dx} = (C_{A0} - C_{Ai}) \sum_{n=1}^{\infty} \frac{4e^{\frac{(2n-1)\pi^2DAt}{4(\delta-\text{Film})^2}}}{2(\delta - \text{Film})} \cos \frac{(2n-1)\pi(x - \text{Film})}{2(\delta - \text{Film})}$$  \hspace{1cm} (D.2)

$$\lim_{x \to \text{Film}} \frac{dC_A}{dx} = (C_{A0} - C_{Ai}) \sum_{n=1}^{\infty} \frac{4e^{\frac{(2n-1)\pi^2DAt}{4(\delta-\text{Film})^2}}}{2(\delta - \text{Film})}$$  \hspace{1cm} (D.3)

$$\frac{dm}{dt} = D_A A \left| \frac{dC_A}{dx} \right|_{x = \text{Film}}$$  \hspace{1cm} (D.4)

$$m = \int_{0}^{t} D_A A \left| \frac{dC_A}{dx} \right|_{x = \text{Film}} \cdot dt$$  \hspace{1cm} (D.5)
\[ m = 4D_A A(C_{A0} - C_{A1}) \int_0^T \sum_{n=1}^{\infty} \frac{e^{-\frac{(2n-1)^2 \pi^2 D'A}{4(\delta - Film)^2}}}{2(\delta - Film)} \cdot dt \]  
\quad \text{(D.6)}

\[ m = \frac{-8(\delta - Film) A(C_{A0} - C_{A1})}{\pi^2} \sum_{n=1}^{\infty} \left[ \frac{e^{-\frac{(2n-1)^2 \pi^2 D'A}{4(\delta - Film)^2}}}{(2n - 1)^2} - 1 \right] \]  
\quad \text{(D.7)}
APPENDIX E

CALCULATING THE FRACTIONAL CONVERSION OF ICE TO HYDRATE

The fractional conversion of ice to hydrate is defined by Equation E.1. Where $m_I$ is the mass of ice in the sample and $m_{I0}$ is the mass of ice that was added at the start of the experiment.

$$\eta = 1 - \frac{m_I}{m_{I0}} \quad (E.1)$$

A volume balance gives Equation E.2. Where $V_G$ is the gas phase volume, $V_S$ is the sample volume, $V_I$ is the ice volume and $V_H$ is the volume of the hydrate phase.

$$V_G = V_S - V_I - V_H \quad (E.2)$$

A mass balance on the hydrate yields Equation E.3. Where $N_G$ is the moles of gas in the hydrate, $M_G$ and $M_W$ are the molecular weights of the gas and water respectively, and $\theta$ is the molar ratio of water to gas in the hydrate.

$$m_H = N_G M_G + \theta N_G M_W \quad (E.3)$$

A mass balance on the water phase yields Equation E.4.

$$m_I = m_{I0} - \frac{m_H M_W \theta}{M_W \theta + M_G} \quad (E.4)$$
A molar balance on the gas phase yields Equation E.5 where \( N_G \) are the moles of gas in the hydrate, \( N_{G0} \) are the moles of gas that were present at the start of the experiment and \( N_t \) are the moles of gas that are currently present in the gas phase.

\[
N_G = N_{G0} - N_Gt
\]  \hfill (E.5)

\( N_{G0} \) can be found using a suitable equation of state with the starting pressure and temperature of the sample and the volume of gas \( V_{G0} \) which in turn can be found from Equation E.2 since \( V_H \) is zero at the start of the experiment and the mass of ice and the volume of the sample are known. However, to find \( N_{Gt} \) the volume balance and mass balance on the hydrate must be solved simultaneously as shown in Equation E.6.

\[
V_G = V_S - V_I - V_H = V_S - \frac{m_H}{\rho_H} - \frac{m_I}{\rho_I}
\]  \hfill (E.6)

\[
N_G = N_{G0} - N_{Gt} = N_{G0} - \frac{V_G}{\nu} = N_{G0} - \frac{V_S - \frac{m_H}{\rho_H} - \frac{m_I}{\rho_I}}{\nu}
\]  \hfill (E.7)

Equation E.8 emerges from substituting Equation E.4 into Equation E.7. The term \( \nu \) represents the molar volume of the gas phase which can be found from an equation of state. By substituting Equation E.8 into E.3, we arrive at Equation E.9.

\[
N_G = N_{G0} - \frac{V_S - \frac{m_H}{\rho_H} - \frac{m_I}{\rho_I} + \frac{m_H M_W \theta}{\rho_I(M_W \theta + M_G)}}{\nu}
\]  \hfill (E.8)

\[
m_H = N_{G0}(M_G + \theta M_W) + \frac{M_G + \theta M_W}{\nu} \left[ \frac{m_H}{\rho_H} + \frac{m_I}{\rho_I} - V_S - \frac{m_H M_W \theta}{\rho_I(M_W \theta + M_G)} \right]
\]  \hfill (E.9)
\[ m_H = \frac{M_G + \theta M_W}{\nu} \left[ V_S - \frac{m_{10}}{\rho_I} \right] - N_{G0}(M_G + \theta M_W) \]  
\[ m_H = \frac{\left[ V_S - \frac{m_{10}}{\rho_I} \right] - \nu N_{G0}}{\left[ \frac{1}{\rho_H} - \frac{\theta M_W}{\rho_I(M_W\theta + M_G)} \right] \frac{\nu}{M_G + \theta M_W}} \]  

Substitution of Equation E.11 into E.4 gives Equation E.12. Hence the hydrate conversion can be found by substitution of Equation E.12 into E.1.

\[ m_I = m_{I0} - \frac{M_W\theta}{M_W\theta + M_G} \left[ V_S - \frac{m_{10}}{\rho_I} \right] - \frac{\nu N_{G0}}{M_W\theta + M_G} \]  
\[ \eta = \frac{M_W\theta}{m_{I0}(M_W\theta + M_G)} \left[ V_S - \frac{m_{10}}{\rho_I} \right] - \frac{\nu N_{G0}}{M_W\theta + M_G} \]