



Methane production via in-situ point heat source thermal stimulation from gas hydrates

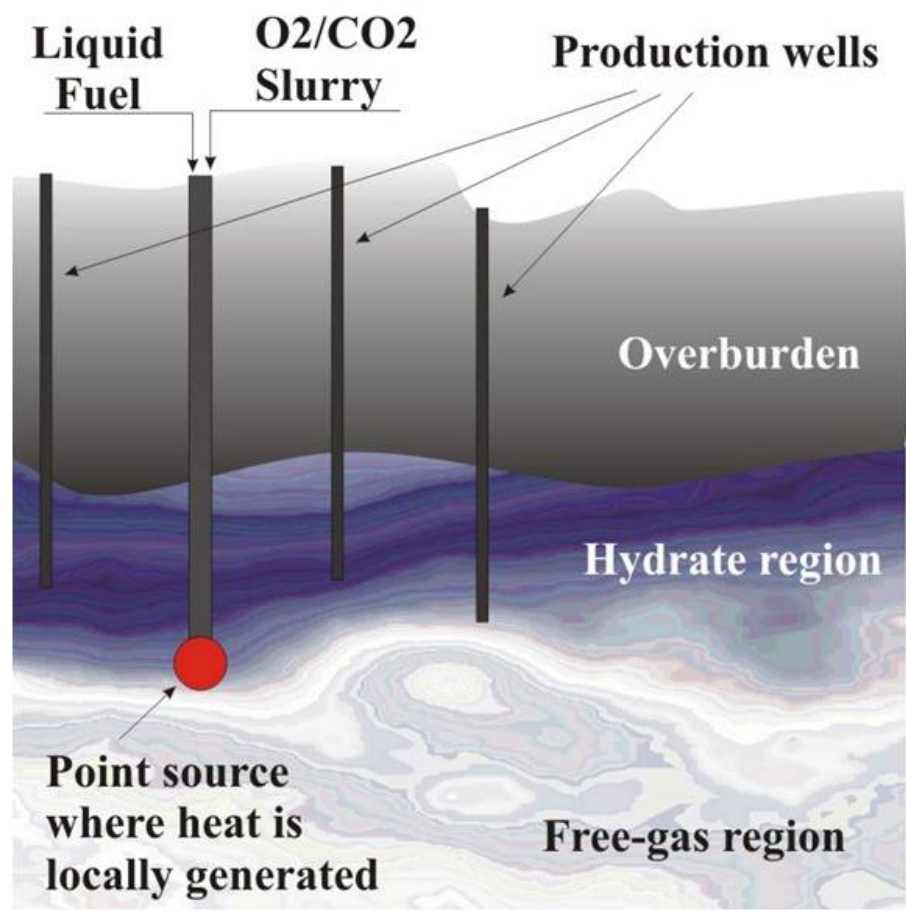
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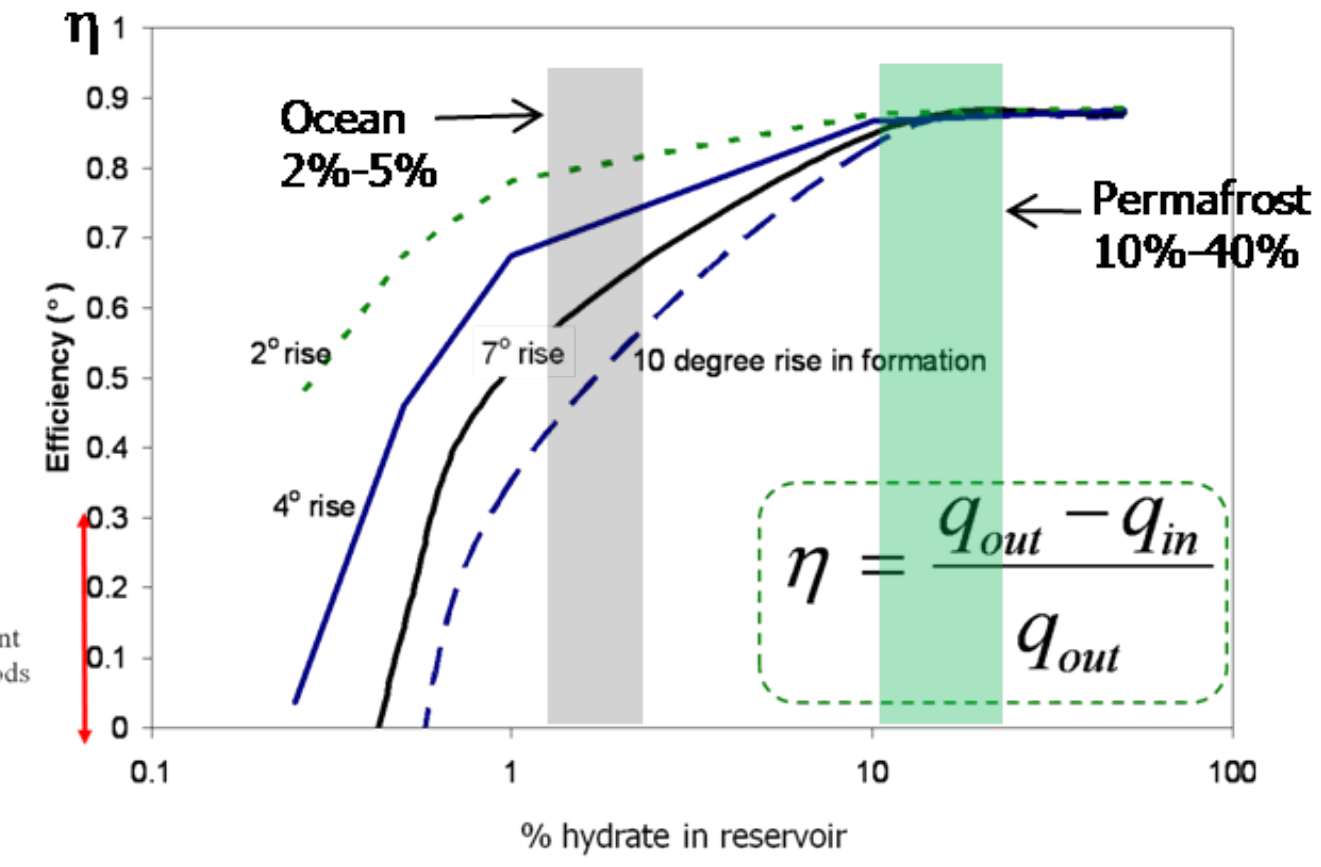


Introduction

Increasing demand for clean and abundant energy sources has motivated the field of gas production from natural hydrate deposits. The global potential of methane stored as hydrates is estimated at twice the net carbon stored in conventional fossil fuels^[1], nearly 10,000 gigatons! This work is focused on the concept of hydrate dissociation for gas production, via in-situ combustion, as a point heat source for thermal stimulation of natural gas hydrate deposits. The basis of this research is in investigating the possibility of using CO₂ as an in-situ thermal diluent during the recovery of methane from hydrates while simultaneously sequestering CO₂ in the thermodynamically and geo-mechanically stable hydrate phase.



Point heat source production method

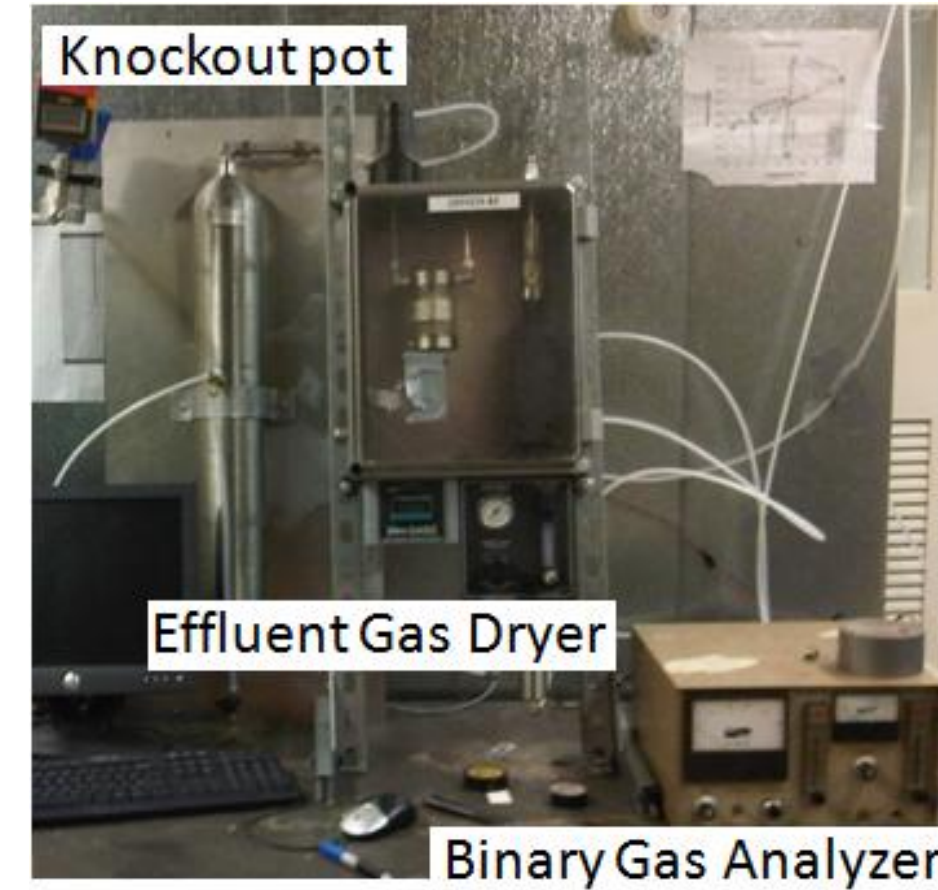


Theoretical efficiencies of hydrate production

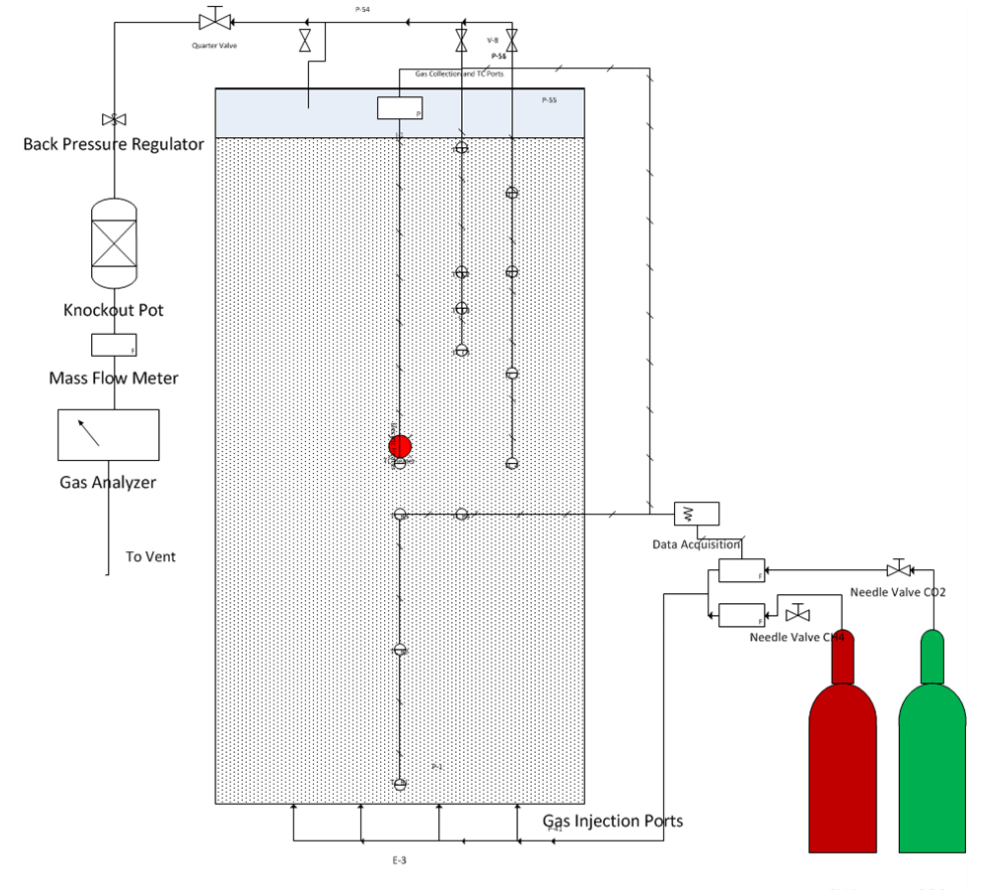
Current production methods include:

1. Conventional thermal stimulation - Not practical without depressurization
2. Formation depressurization- Inconsistent flow rates and self preservation effect
3. Chemical inhibitor injection-Potentially costly and environmentally un-friendly

Experimental Apparatus



Gas analysis and drying system



Experimental setup

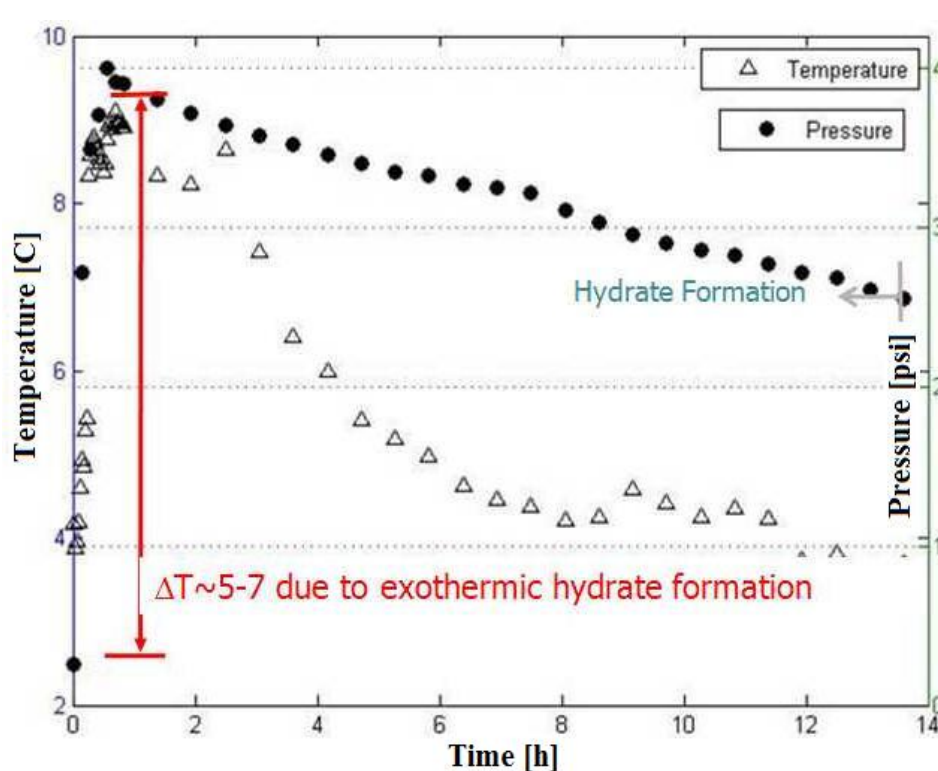


70 liter high pressure reactor

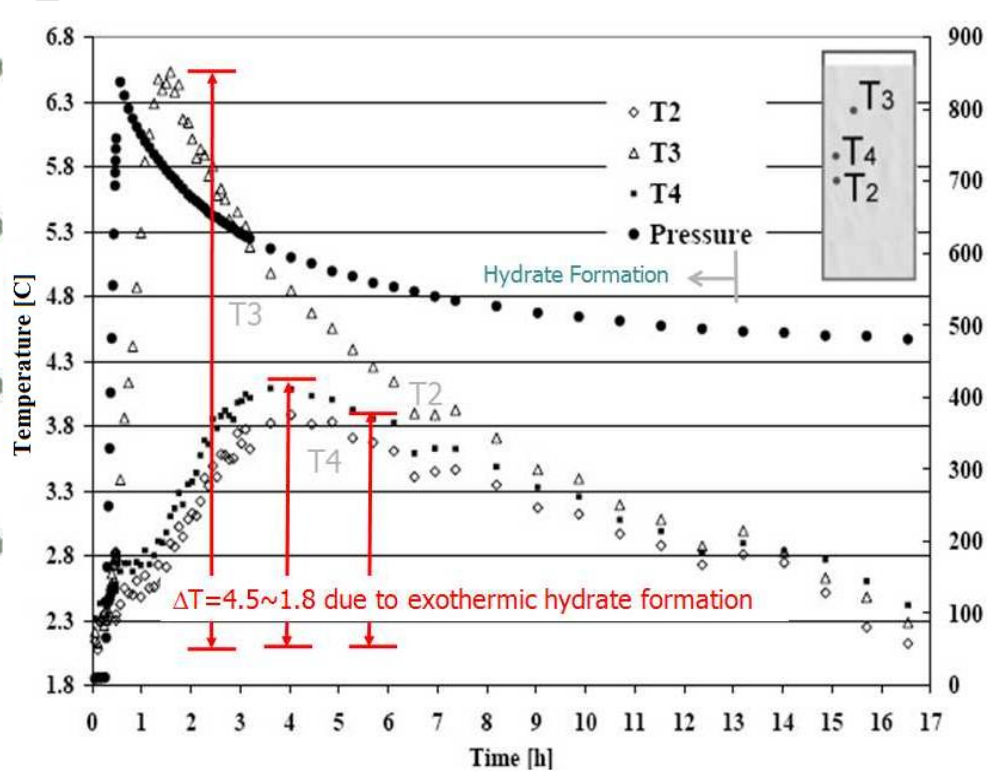
Apparatus Capabilities

- Pressure 0-1000 psi • Temperature -8 -20 °C • 13 K-type Thermocouples
- 1 pressure transducer [0-10,000 psi] • Online Binary TCD gas analyzer
- 250 watt resistive heater • Quartz sand 100-500 μm • Porosity ~ 30 %
- 4 liter knockout pot for water recovery

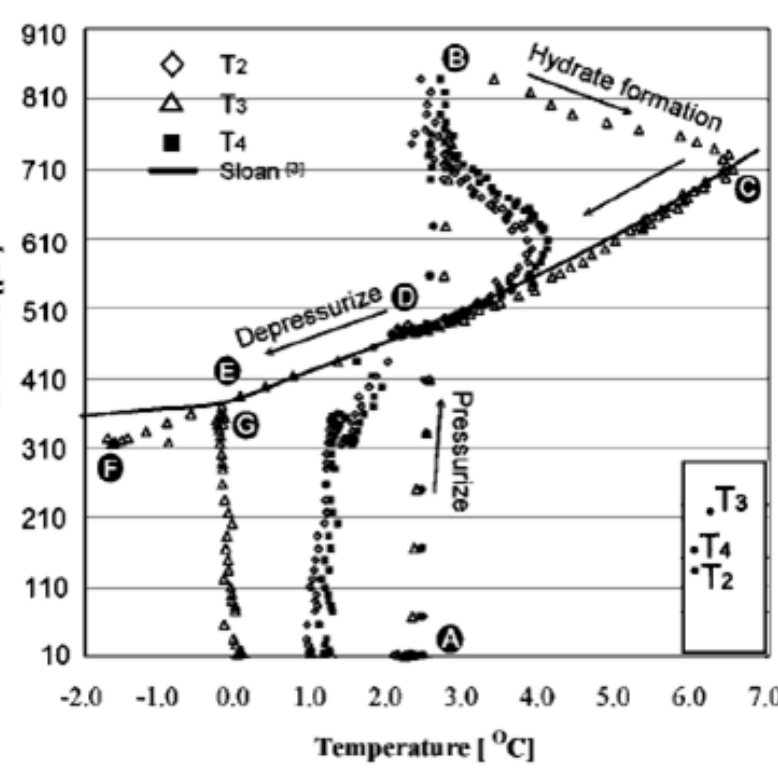
CO₂ and CH₄ Hydrate Formation



CO₂ hydrate formation and exotherm



CH₄ hydrate formation and exotherm



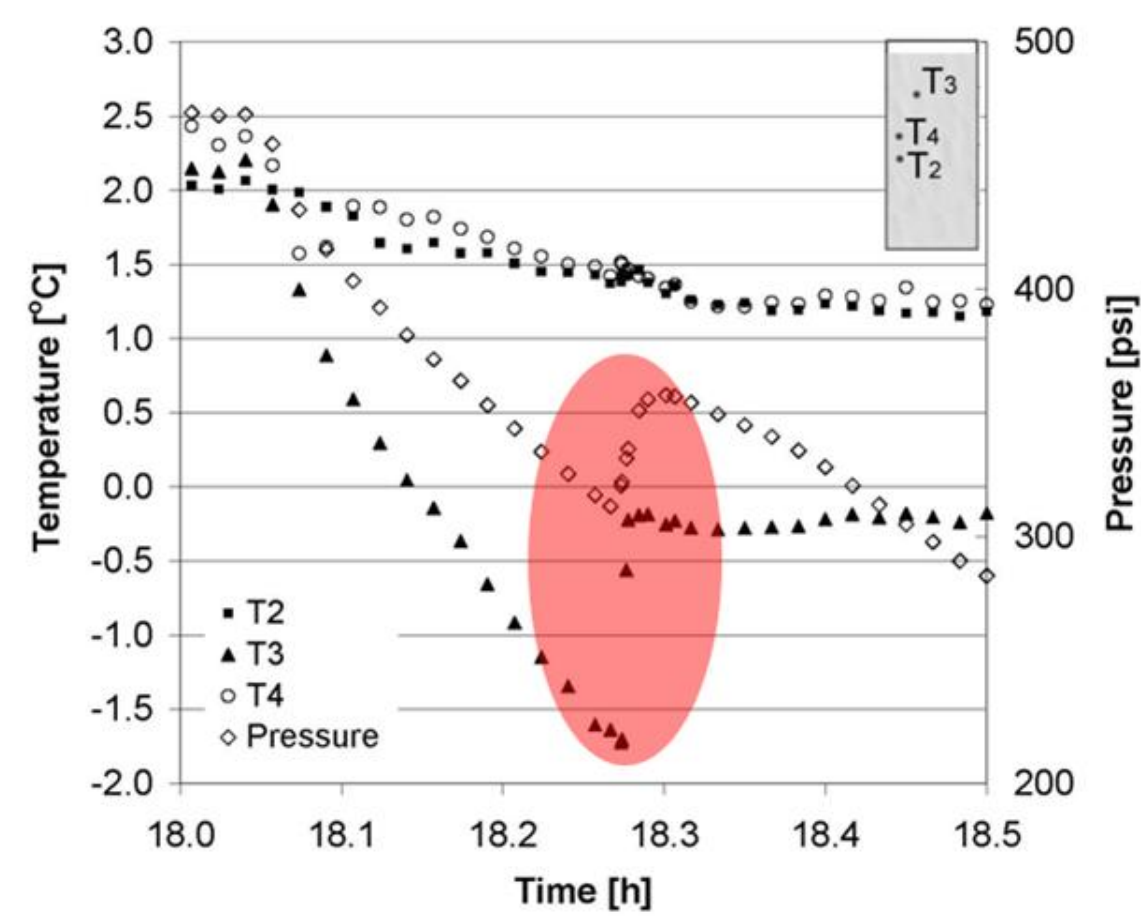
P vs. T during injection, formation and depressurization

- Exotherms and pressure reduction used as primary indication of hydrate formation
- CO₂ exotherm > CH₄ exotherm: Indicating favorable thermodynamics
- ~14-24 hours for L_w-H-V equilibrium to be realized

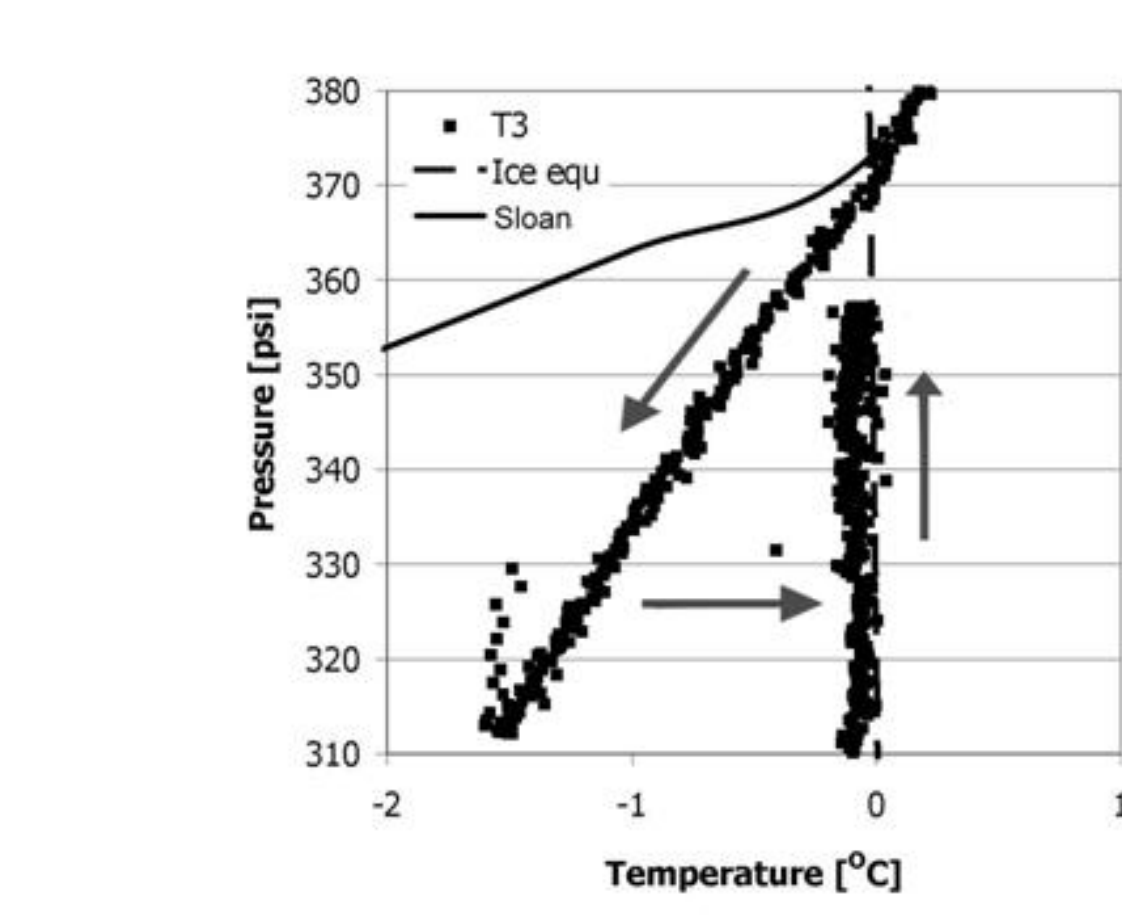
These are typical pressure and temperature results during gas injection demonstrating initial exotherm and pressure reduction followed by a close trace of literature reported equilibrium values for CH₄ hydrates in porous media, confirming hydrate formation. Values diverge slightly just below the ice point indicating sub-cooling prior to a rapid jump to 0 °C as show in the right hand figure.

Recent Findings

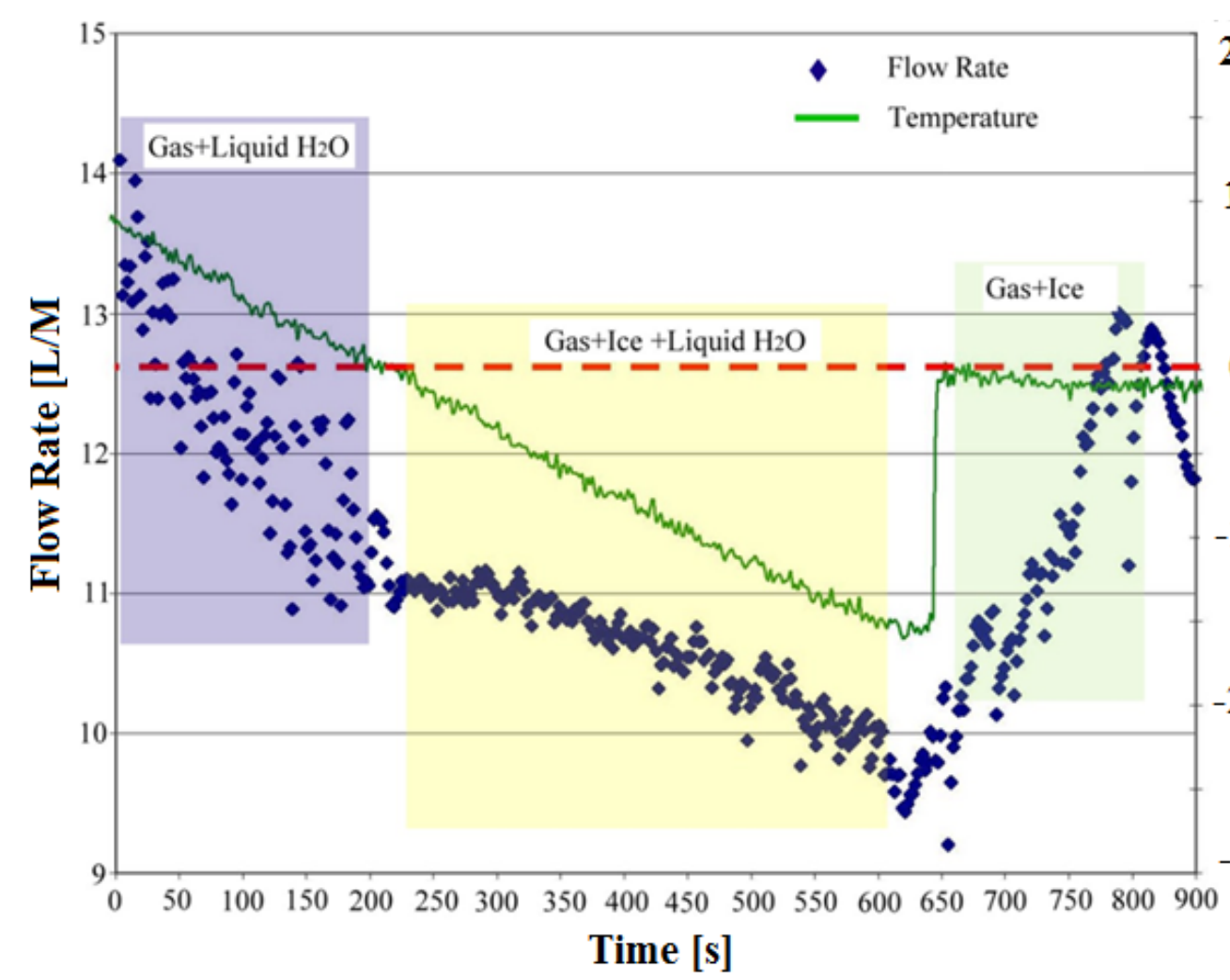
From an analysis of gas recovery volumes, it was concluded that there is a transition regime, characterized by a sharp increase in gas recovery rate as the gas production well pressure decreases and temperatures pass below the ice point. Experimental results produced from this apparatus were the first reported to experimentally observe this transition regime with a mechanistic interpretation. This finding is a useful guide for gas production operations in industrial settings. The transition regime can be used to avoid accidents during production or to increase the gas production rate in the field



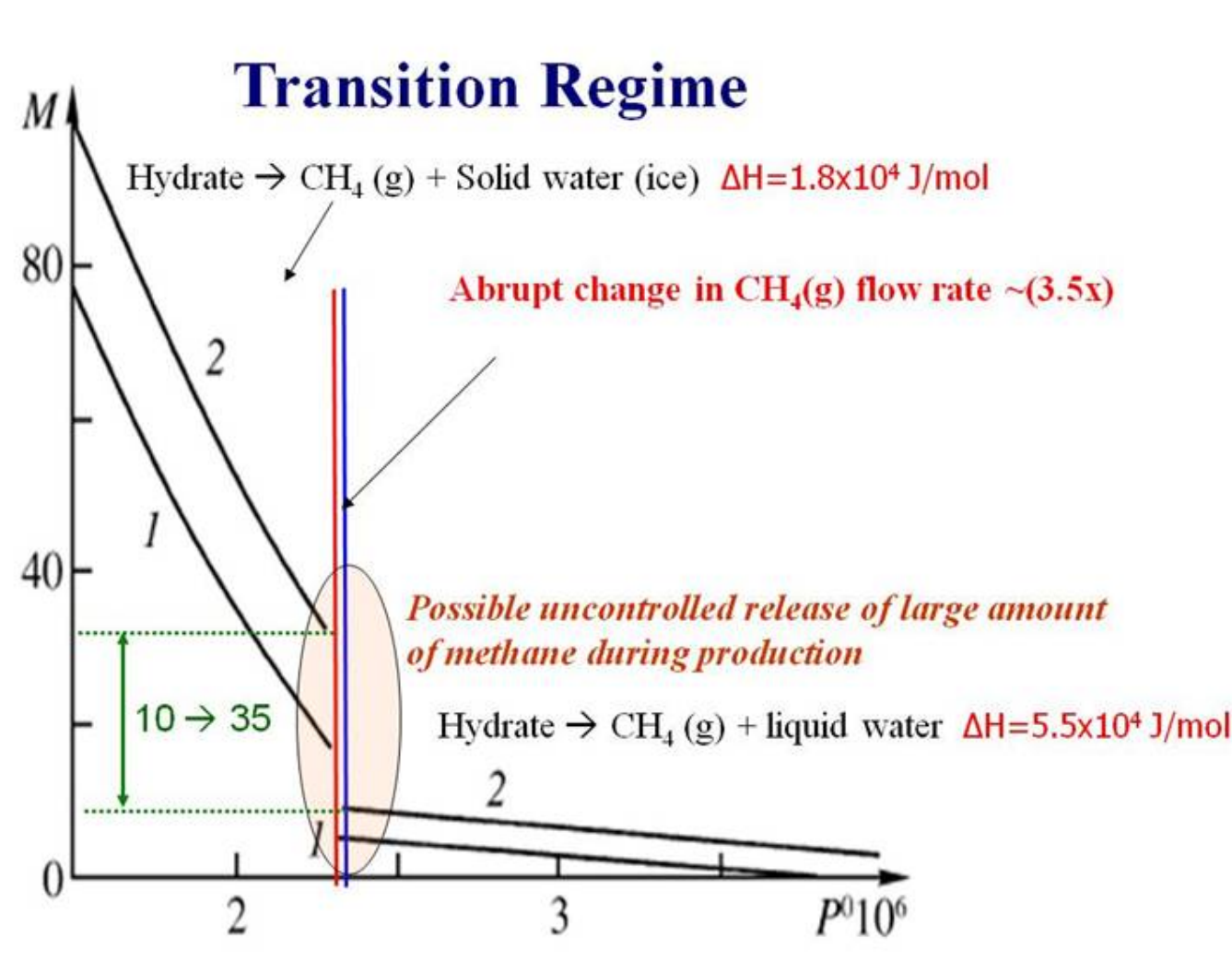
Ice formation and pressure spike during transition regime



Deviation from equilibrium during transition regime



Transition regime during dissociation with gas production increase ^[2]

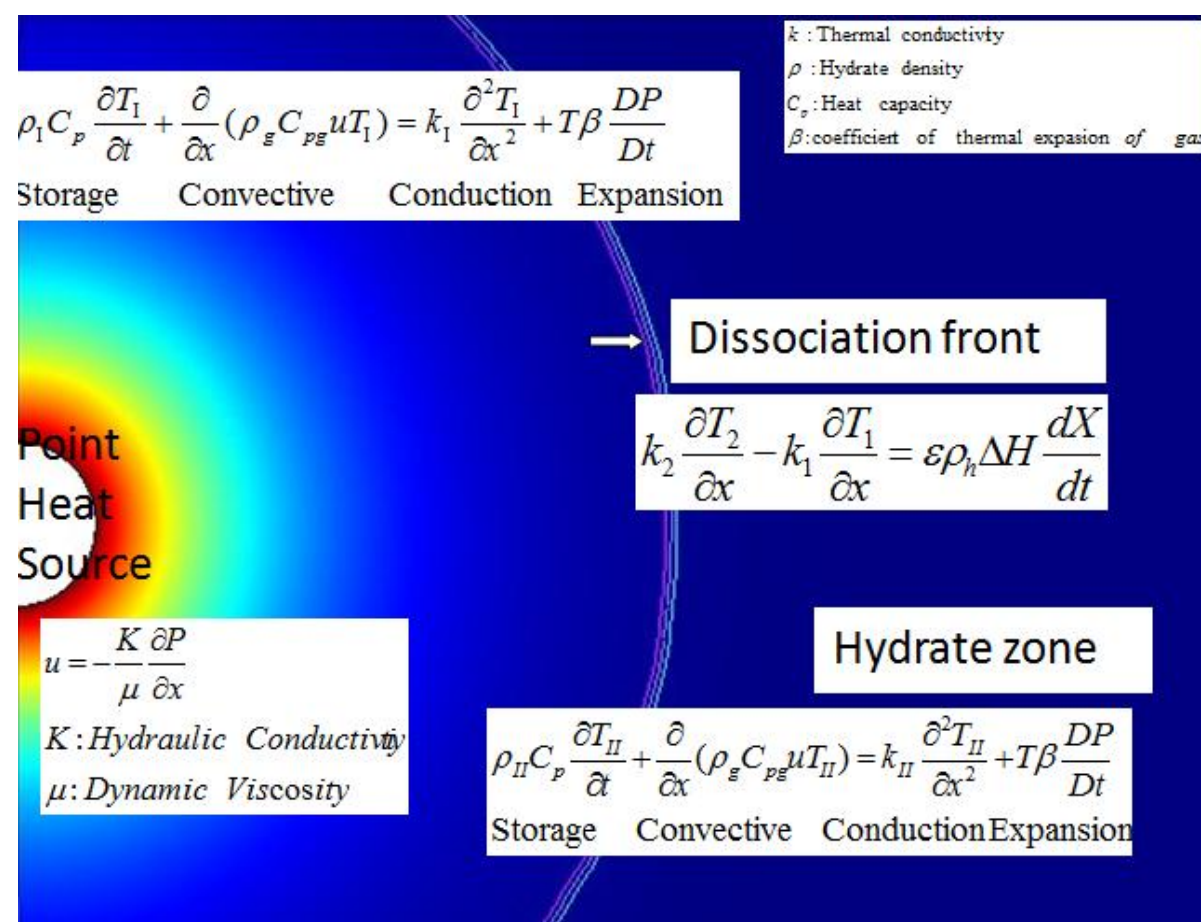


Proposed gas production curves from Tyspink^[3]

The depressurization data shows ice formation in the system coinciding with an abrupt increase in mass flow and pressure when the temperature drops below 0 °C indicating subcooling. This is in agreement with the results proposed by Tyspink shown in the figure where a transition regime of dissociation to both water and and ice exists. It is proposed that this increase flow results partially from the three fold decrease in the enthalpy of dissociation of hydrate to ice compared to water. However it is likely that in industrial applications this ice formation will cause inhibited flow issues do to the very low permeability of ice.

Computer Simulation

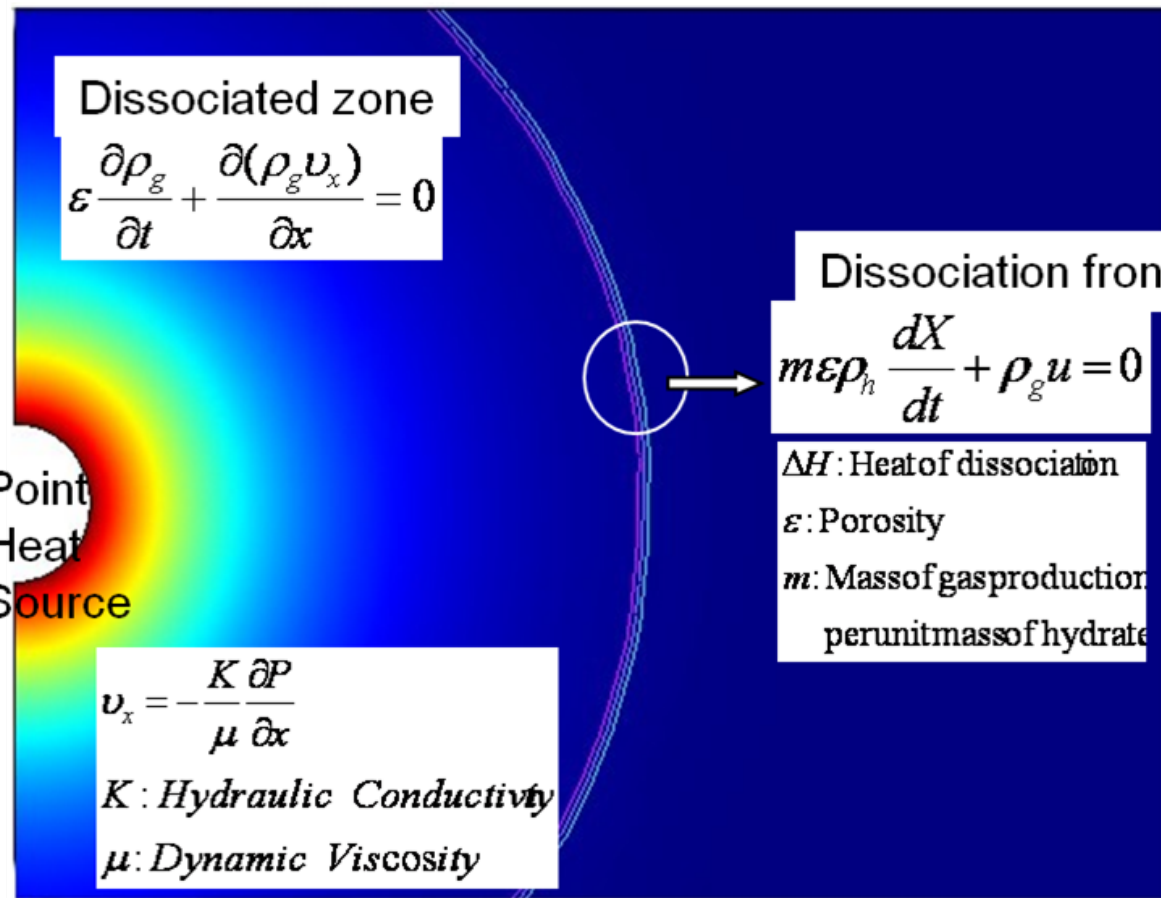
The COMSOL model has been developed from first principles using coupled heat and mass balance equations. Darcy's law is the governing constitutive equation for movement of material though the matrix.



Energy Balance separated into three coupled regimes

1. Dissociated Zone
2. Dissociation front
3. Stable Hydrate Zone

Conductivity, Density, and Heat capacity are adjusted via a smoothed Heaviside step function



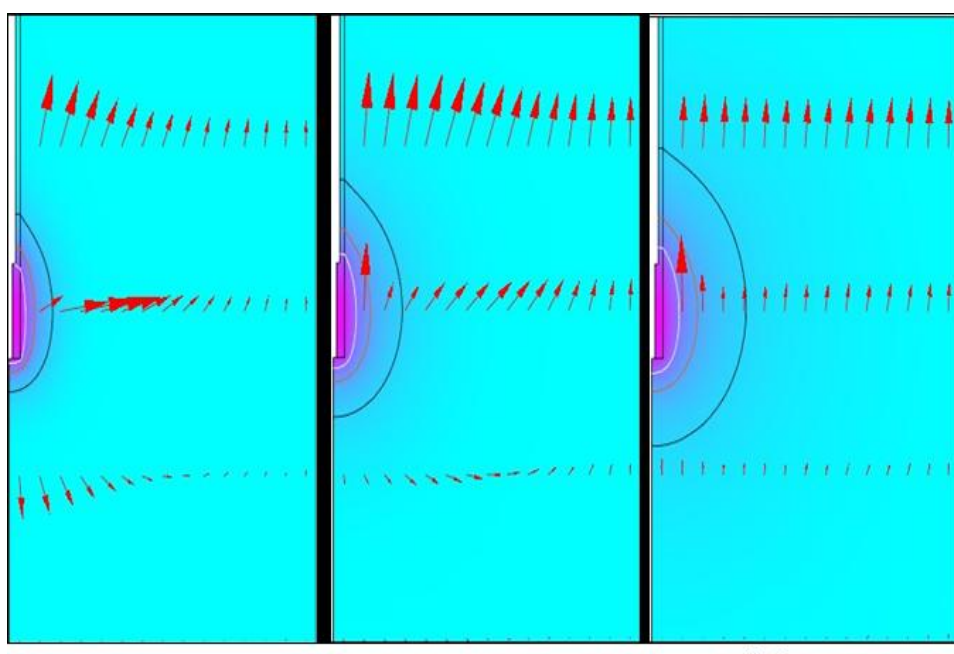
The mass balance is also separated into the three different phases.

Permeability of Hydrate zone is roughly 1000 times less than dissociated zone explaining the mass transfer limitation issues associated with secondary hydrate formation. Both permeability and porosity are adjusted similarly as thermal properties via Heaviside step function.

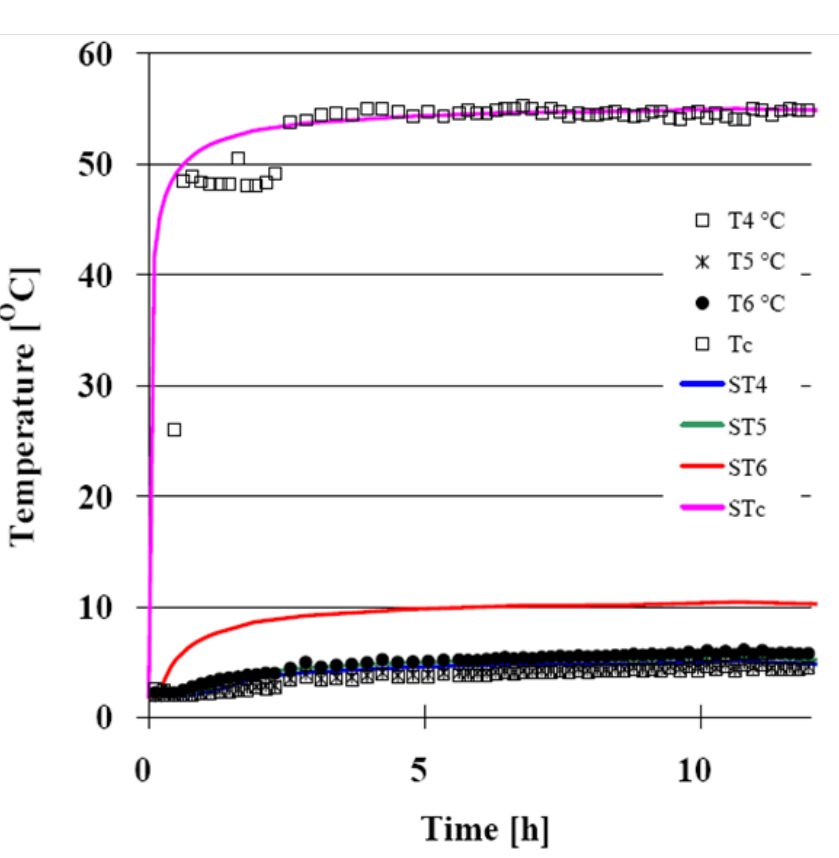
Due to non-linearities and complex coupling associated with the kinetic parameters in this simulation all phase changes are currently represented as a step transitions, via a Heaviside function governed by thermodynamic equilibrium values taken from experimental data and the literature. Where the phase property is defined as below:

[Hydrate property](1-flc2hs(x,y))+[Dissociated zone property](flc2hs(x,y)) where Ts is the equilibrium temperature at a given pressure and flc2hs(x,y) is a COMSOL function that creates a smoothed Heaviside function at 'x' with a width of 'y'

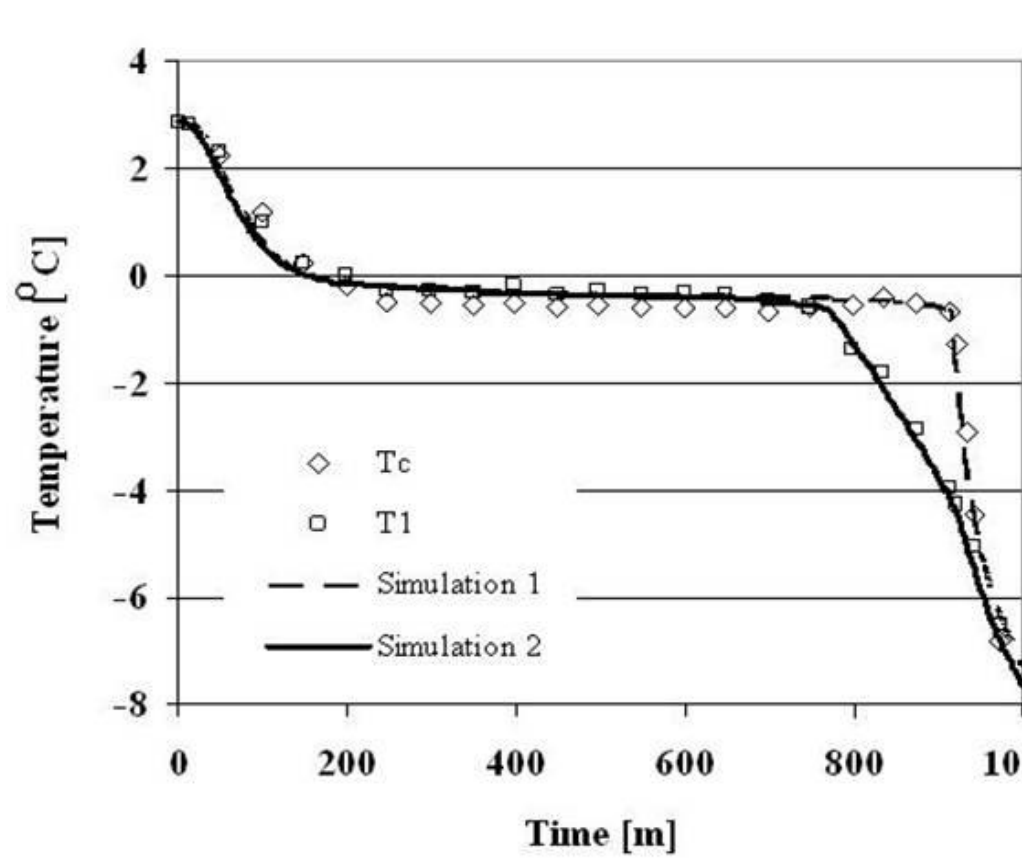
Model Results and Verification



Gas evolution during heating simulation

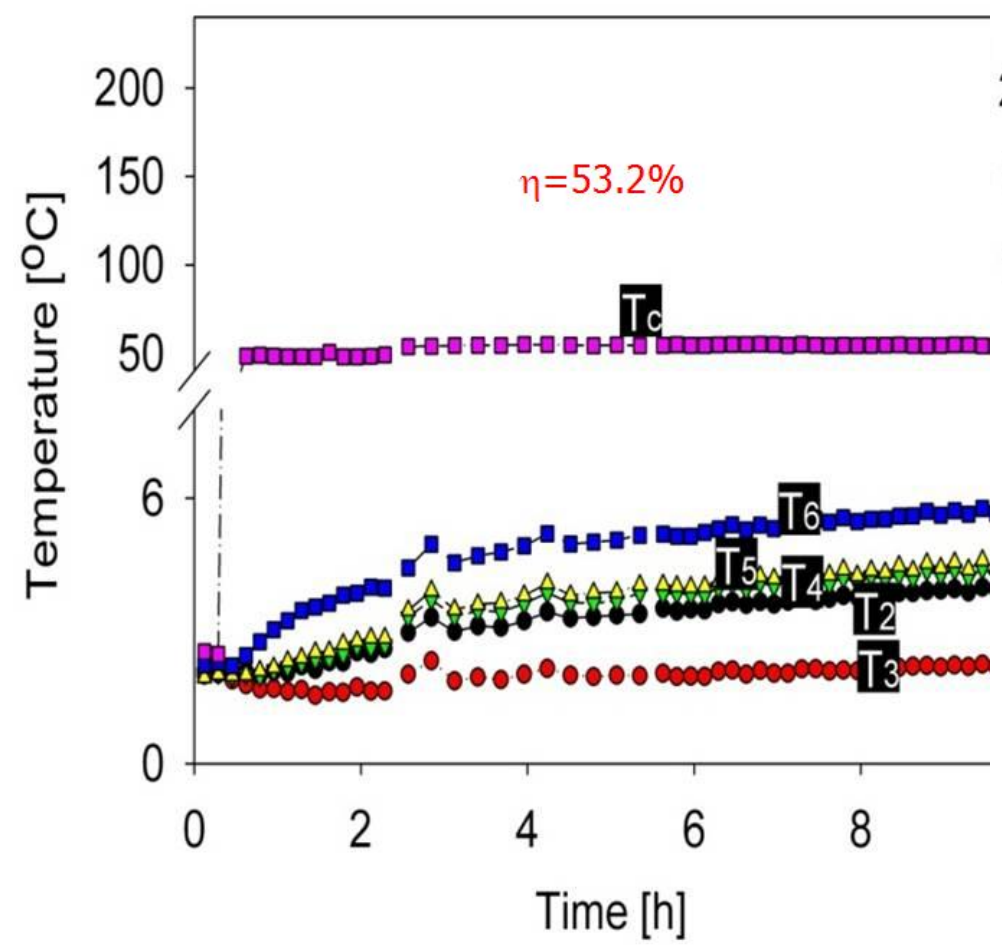


Temperature trace of low heating simulation: experimental and simulation data

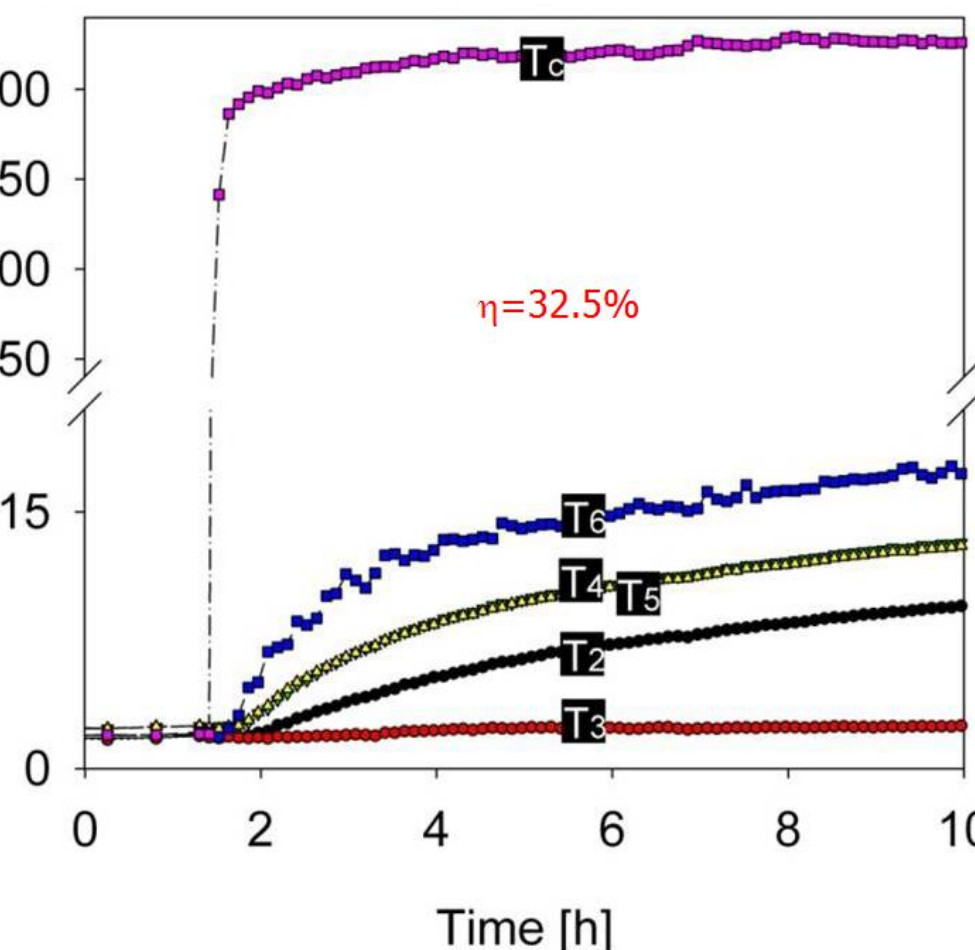


Ice formation: experimental and simulation data

The model can capture the flow of CH₄ through the matrix as hydrate decomposes. The time evolution panels show how as the heat front moves through the matrix the gas initially expands in all directions and eventually moves upwards towards the low pressure region of the well head. The figure to the right was used for verification of thermal properties and the Heaviside step function approach. Experimental temperatures match well with the model prediction.



Experimental data from low heating rate (15.6 watts)



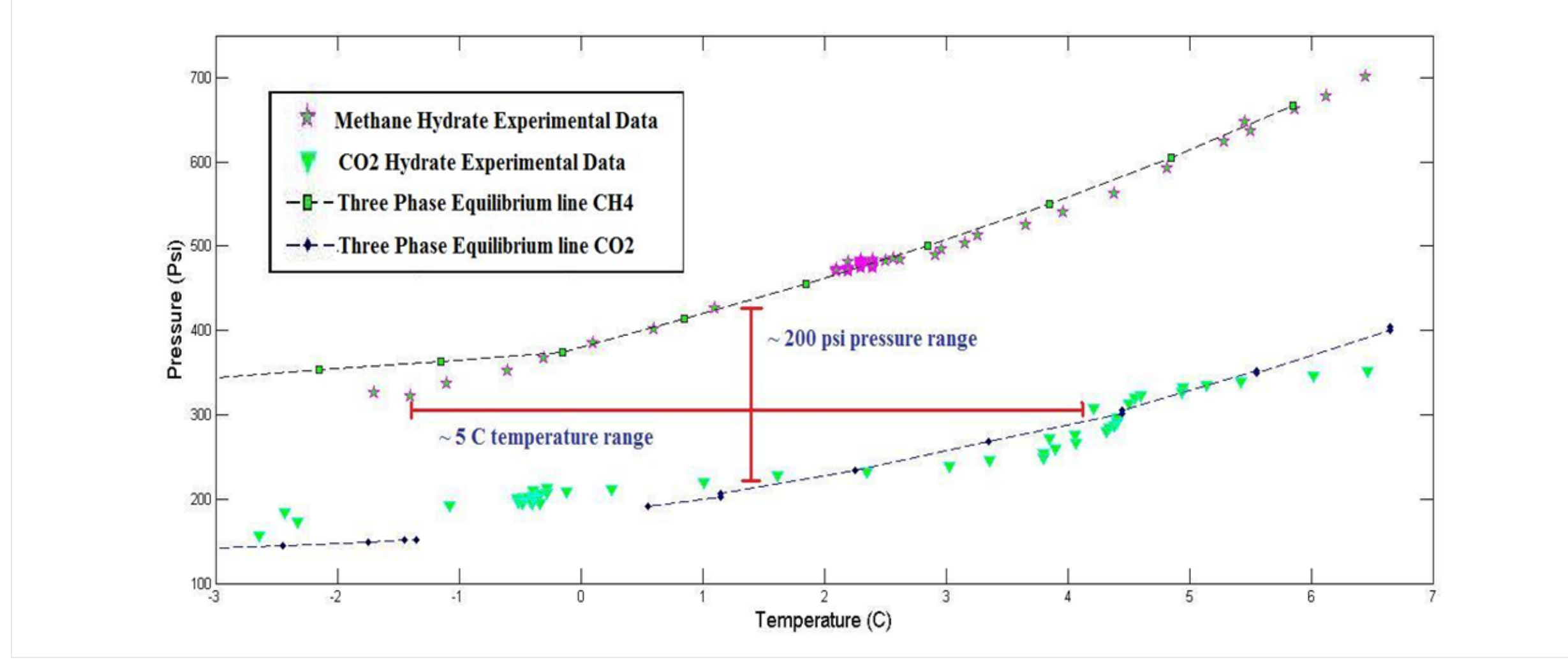
Experimental data from high heating rate (62.5 watts)

Run	Hydrate loading	η
T=1000 °C	0.2	0.72
T=1000 °C	0.5	0.52
Qin= 4 KW	0.1	0.92
Qin= 4 KW	0.2	0.90
Qin= 4 KW	0.5	0.74
Qin= 40KW	0.2	0.42

Summary of various heating scheme simulation results

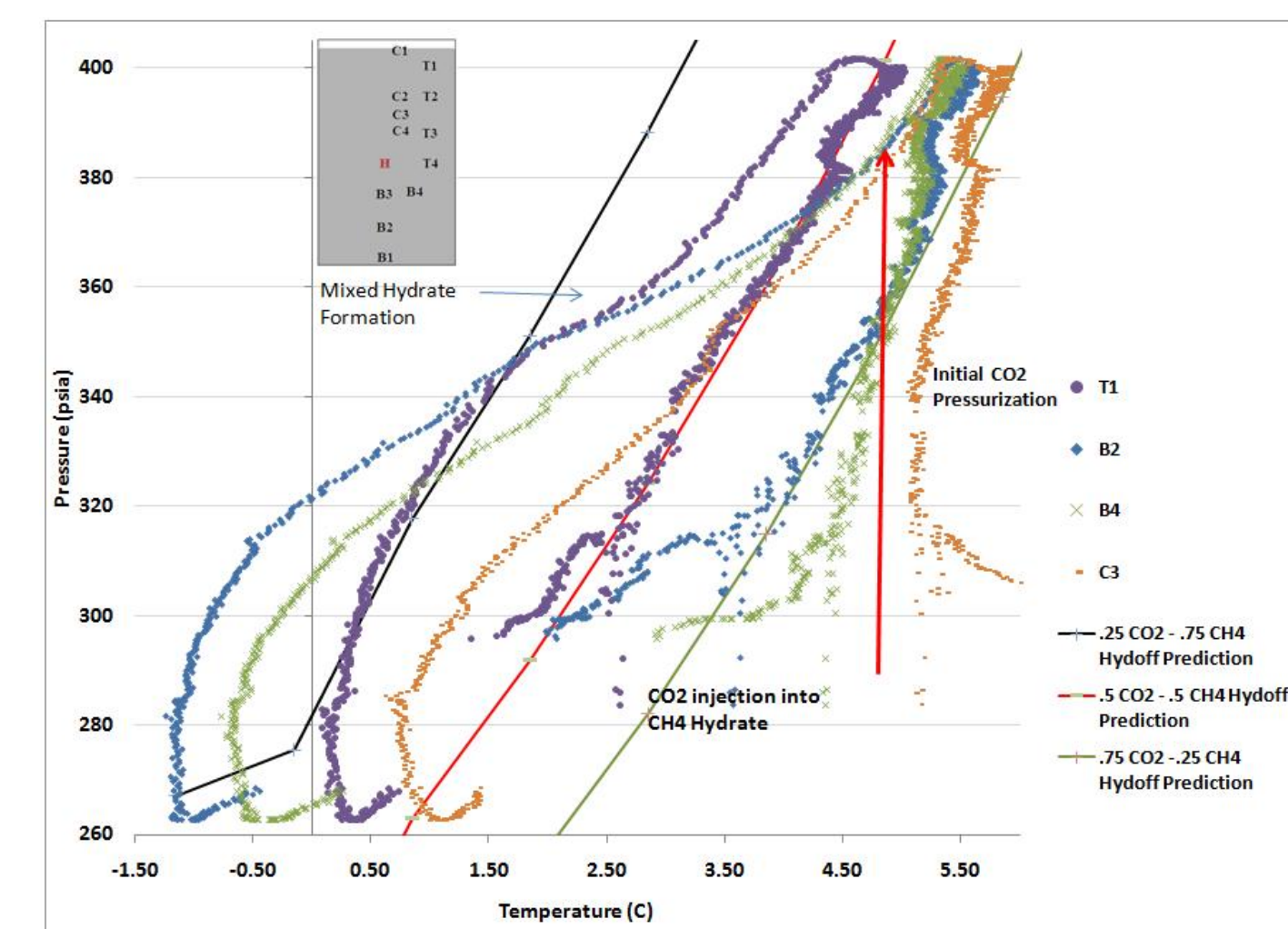
The salient finding is that lower hydrate loadings and low heat rates are associated with increased recovery efficiency. This is because heat energy put into the well can be efficiently used only if it has potential to spread throughout the formation. Higher loadings produce more water that absorbs large amounts of heat. In the case of constant heat flux, heat energy is input slowly such that there is no major accumulation of heat at the source. Lower experimental heating rates tend to result in slower production rates at higher efficiencies. Higher heating rates show increased energy losses due to excessive sediment heating as a result of heat transfer limitations.

CO₂ sequestration potential

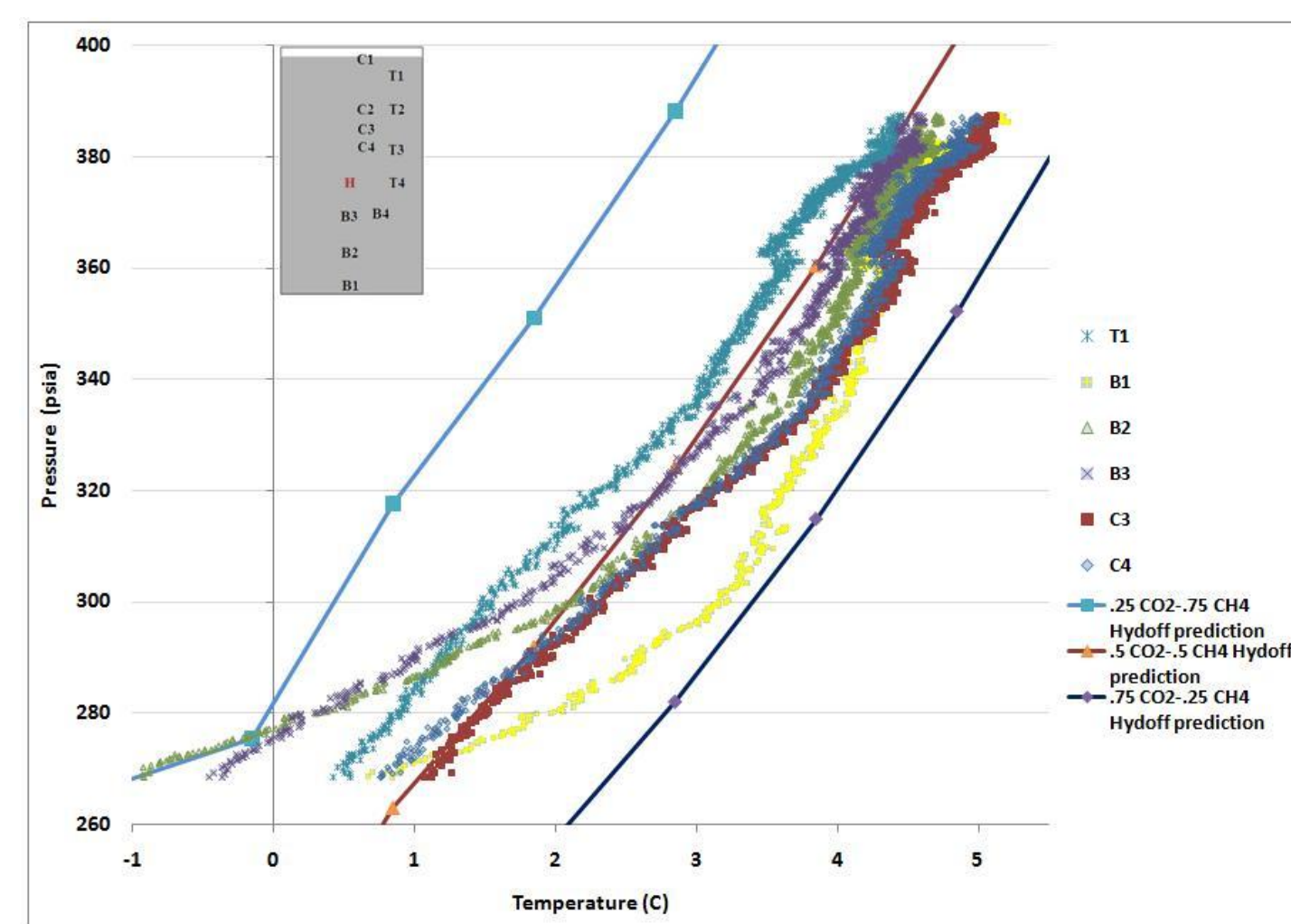


CO₂ sequestration envelope as demonstrated in our apparatus in agreeance with by Sloan et al

- H_{dissociation} CO₂ [~57 kJ/mol]> H_{formation} CH₄ [~54 kJ/mol] ie. favorable thermodynamics
- Conserved structural stability of formation when guest CH₄ is replaced with CO₂
- Potential for nearly carbon neutral energy production



Initial injection of CO₂ into mixed CH₄ hydrate and free CH₄ gas



Mixed gas hydrate dissociation during slow warming

A mixed gas hydrate was formed by the injection of CO₂ into previously formed CH₄ hydrate and free gas at a molar ratio of ~1:1. Initial injection (left) follows the equilibrium values for higher CO₂ concentrations while secondary dissociation (right) more closely traces the equi-molar equilibrium line as predicted via the CSMHyd software^[4] High cooling rates present during initial hydrate formation causing the lower temperatures during formation.

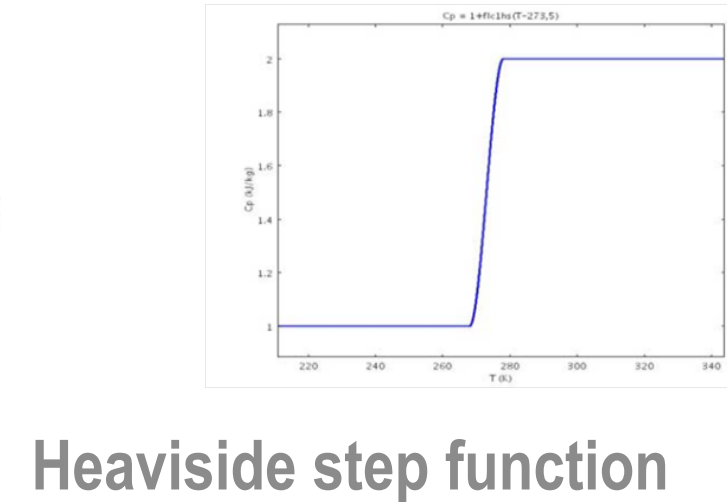
Future Direction

Further development of the model will include coupling of simplified kinetic parameters based on temperature or fugacity deviation from equilibrium values. Depending on the temperature regime and porous media characteristics the system may be controlled by either heat and mass transfer or kinetics. The current method of variable switching does not allow for the investigation of relative kinetic and transfer rates that need to be understood for field production. The apparatus has recently been upgraded for multi-gas injection for continued experimental exploration of CO₂- CH₄ exchange methods.

$$-\frac{dn}{dt} = k_d A_{hs} (f_e - f_g) \frac{m_H}{\phi_H A} = 6.464 \times 10^{14} (\Delta T)^{2.05}$$

Kim & Bishnoi (1989) ^[6]

Kamath (1984) ^[5]



Heaviside step function

- Investigation of CO₂-CH₄ exchange rates and parameters
- Heating test with in-situ CO₂ injection as a convective thermal transport mode
- Confirmation of hydrate distribution in the matrix
- Evaluation of production characteristics of different rock matrix
- Implementation of combustion source
- Kinetic coupling in COMSOL model
- Extension of Darcy's law to include the Brinkman equation to match flow near the well

Acknowledgments

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References

1. USGS
2. Zhou, Y.; Castaldi, M.J.; Yegulalp, T.M., "Experimental investigation of methane gas production from methane hydrate": Industrial & Engineering Chemistry Research 2009, 48, 3142–3149
3. G.G Tyspink , Russian Academy of Sciences Fluid Dynamics, Vol. 40, No. 1, 2005, pp. 117–125.,
4. Sloan, E. Dendy. CSMHYD.EXE; FEED.DAT; HYDK.EXE; SRKH&S.EXE; SRKH&S.FOR; DOSXMSF.EXE
5. Kim. H.C. Bishnoi, P.R., Heidemann, R.A. Rizvi. S.S.H. 1987 Kinetics of methane hydrate decomposition. Chemical Engineering Science 42
6. Kamath, V., 1983. Study of Heat Transfer Characteristics During Dissociation of Gas Hydrates in Porous Media. University of Pittsburgh, Pittsburgh, PA.