Advances in Avoiding Gas Hydrate Problems

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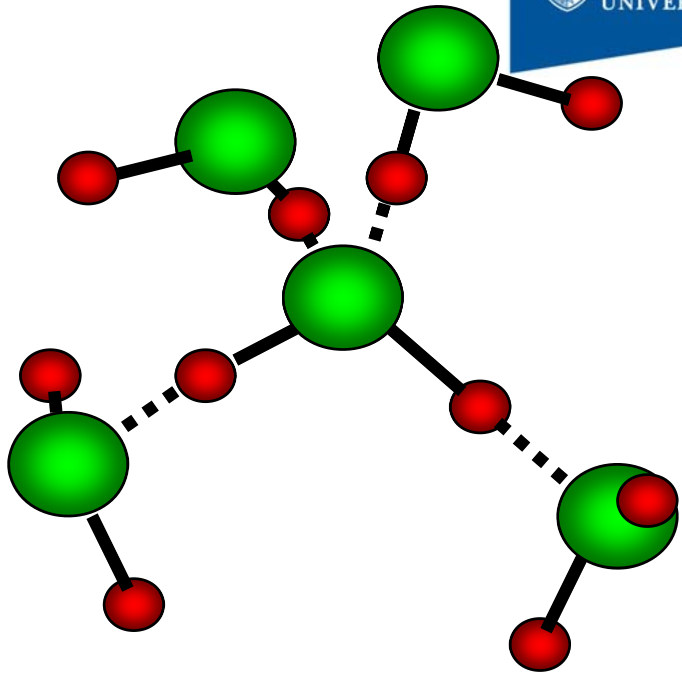
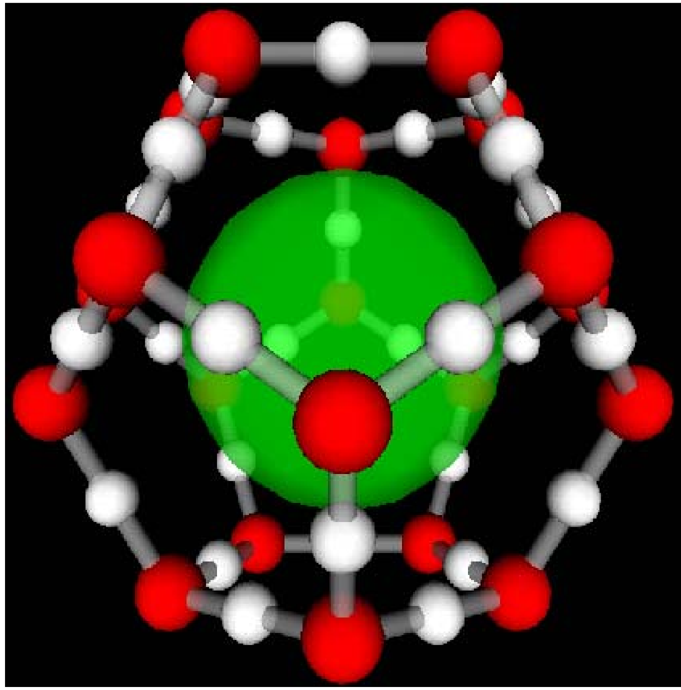
What Are Gas Hydrates?

- Hydrates are crystalline solids wherein guest (generally gas) molecules are trapped in cages formed from hydrogen bonded water molecules (host)
- They look like ice, but unlike ice they can form at much higher temperatures
- Presence of gas molecules give extra attraction, hence stability, fixing the position of water molecules, i.e., freezing at temperatures higher than 0 °C





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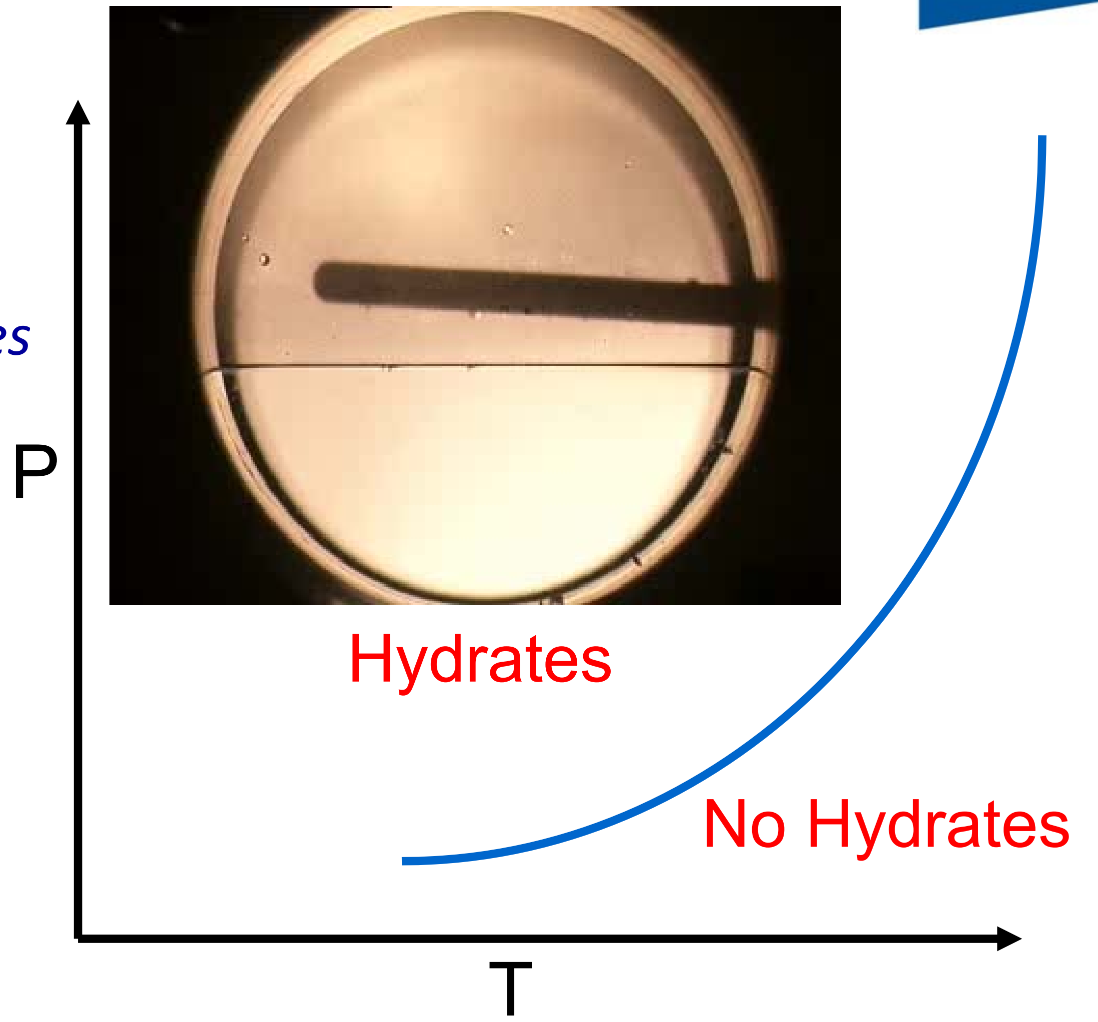
Necessary Conditions

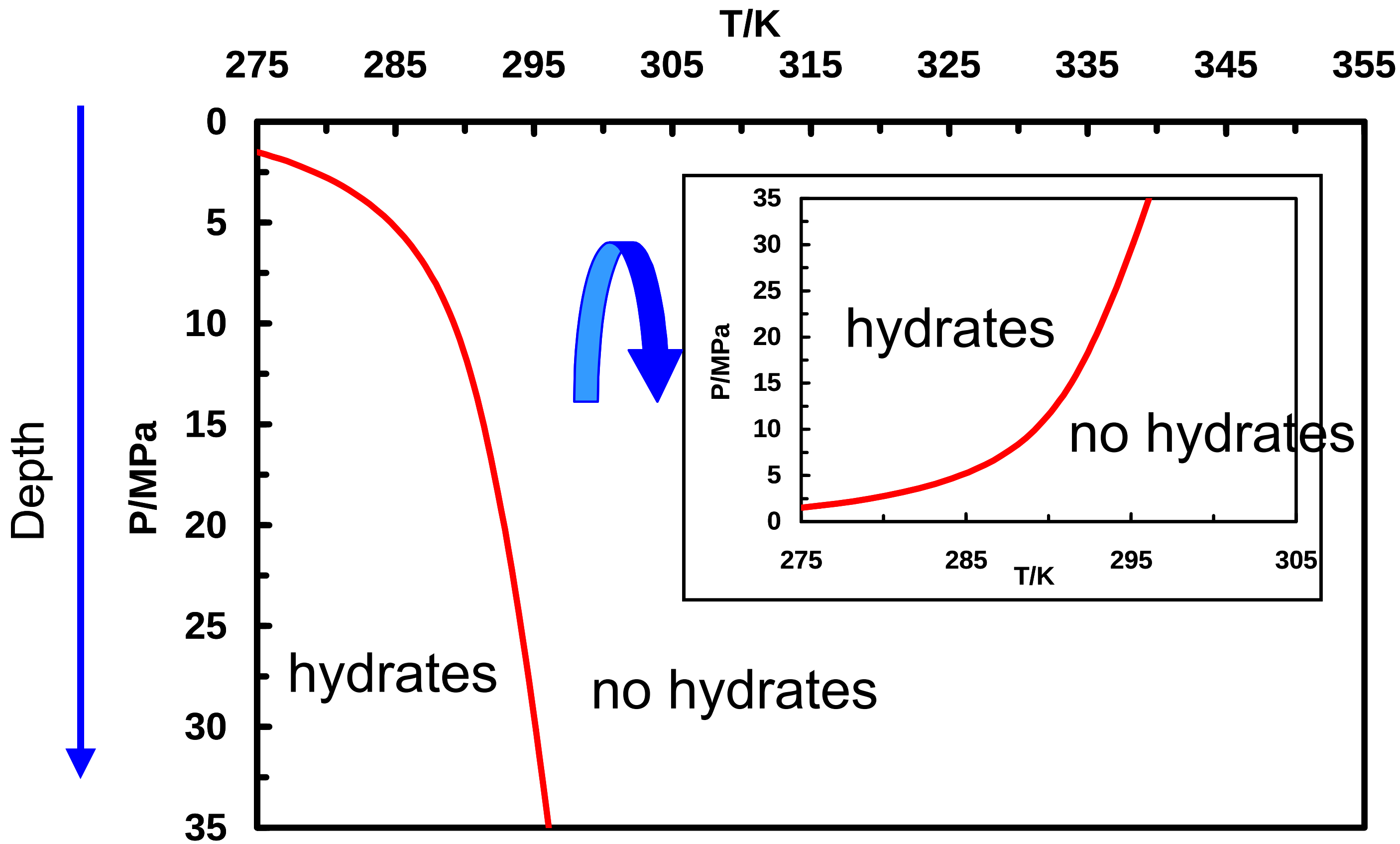
- The necessary conditions:
  - Presence of water or ice
  - *Suitably sized gas/liquid molecules* (such as C_1, C_2, C_3, C_4, CO_2, N_2, H_2S, etc.)
  - Suitable temperature and pressure conditions
- Temperature and pressure conditions is a function of gas/liquid and water compositions.



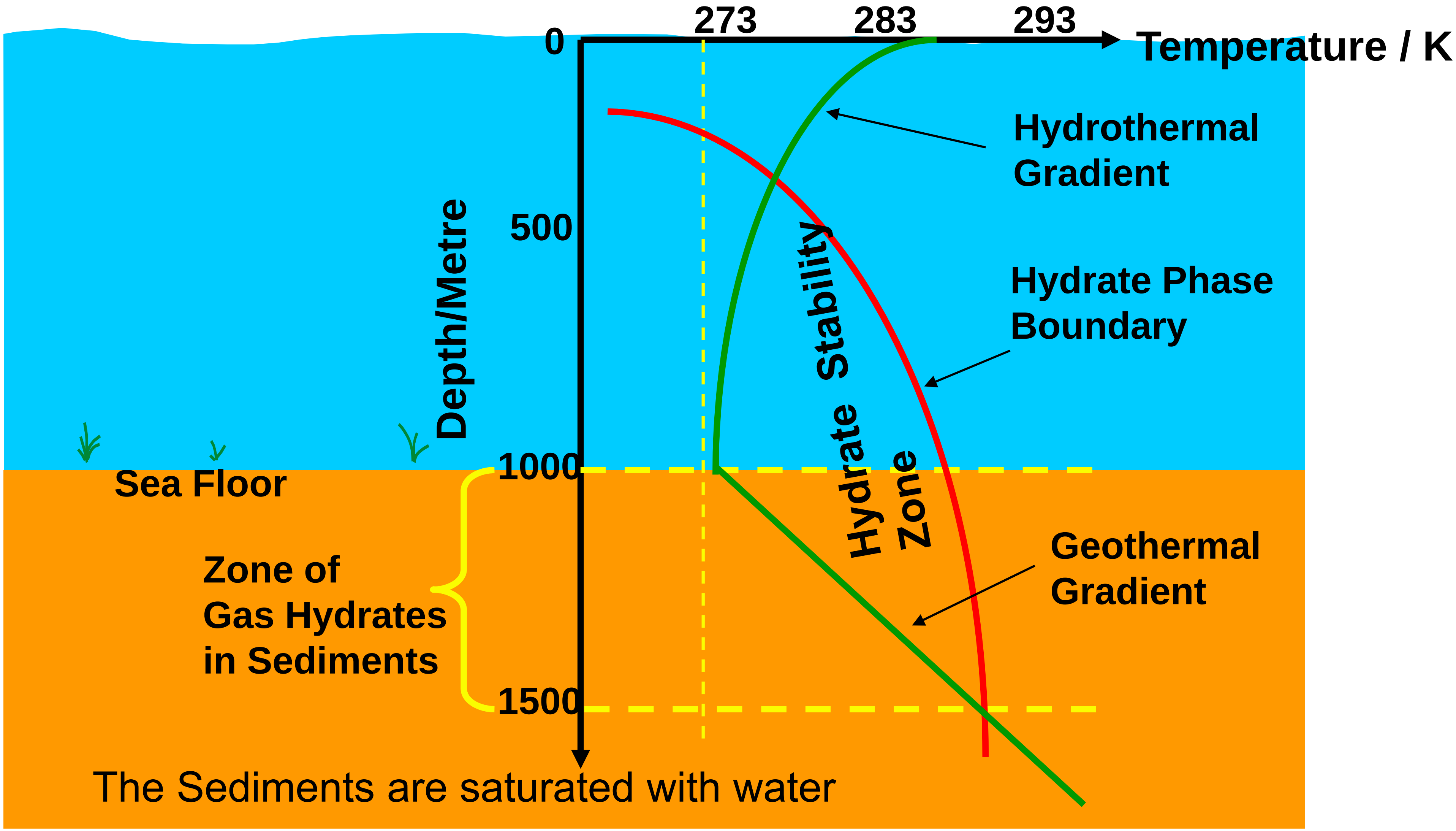
Hydrate phase boundary

Hydrates in Subsea Sediments

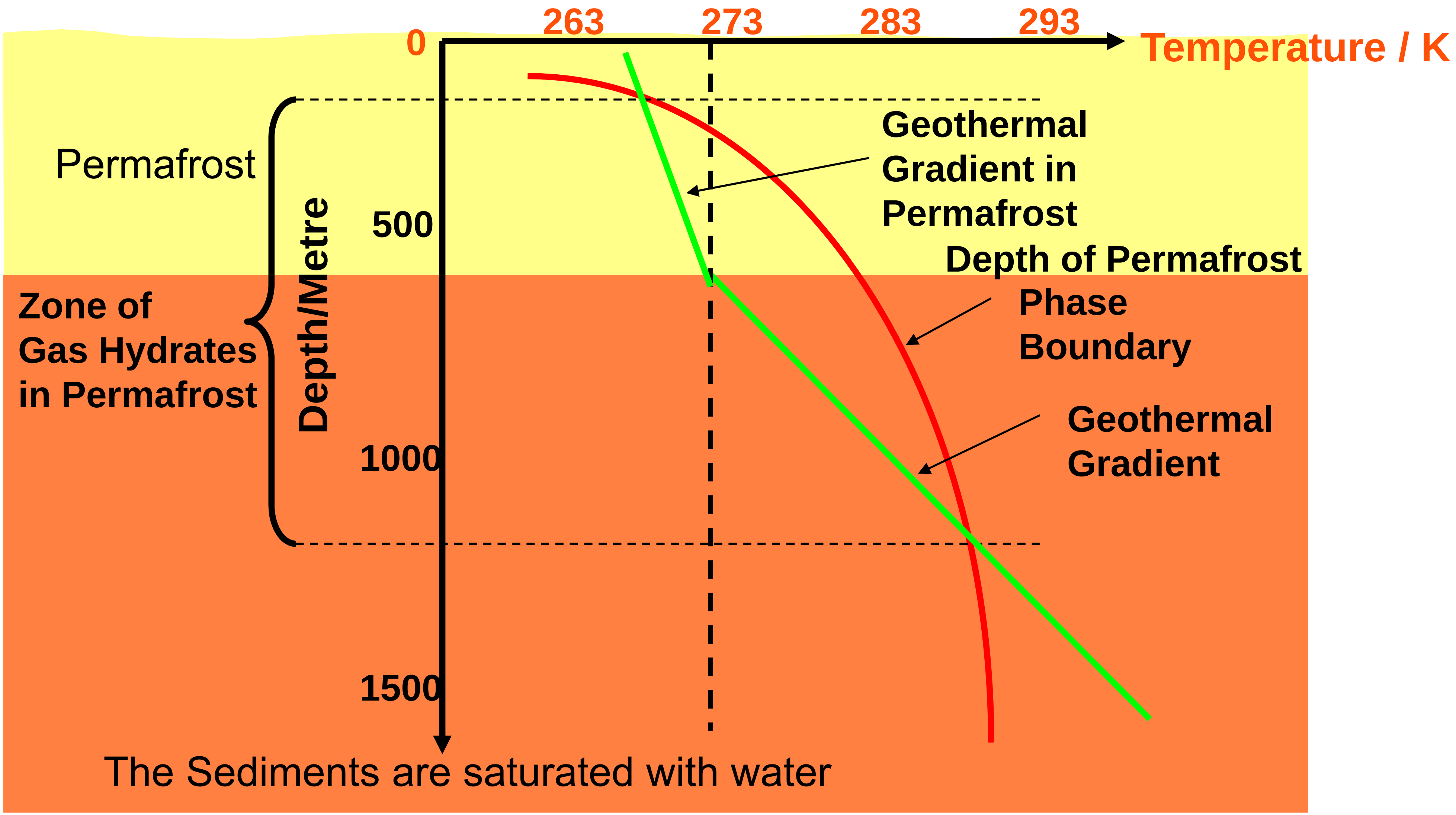
- There are massive quantities of gas hydrates in permafrost and ocean sediments.



Hydrate Stability Zone in Subsea Sediments



Hydrate Stability Zone in Permafrost



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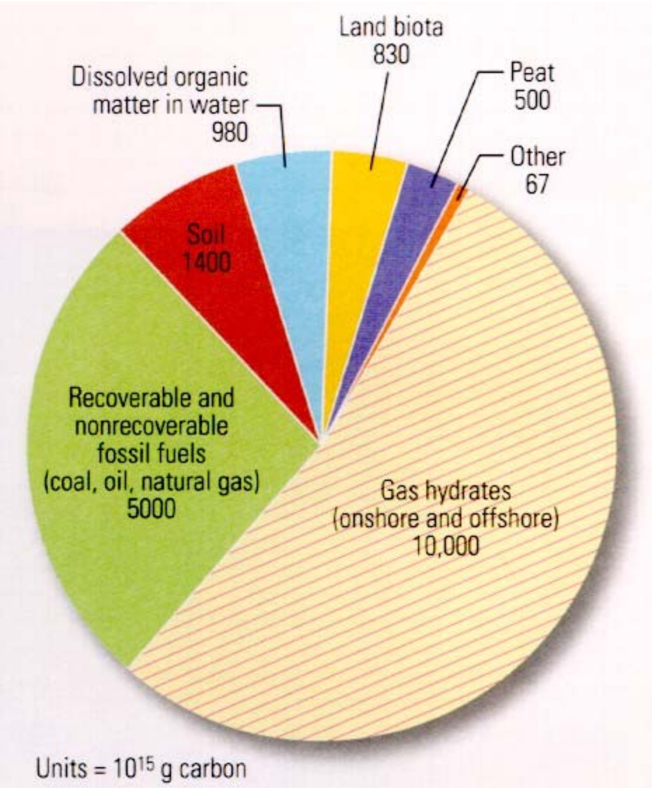
Methane Hydrate Discoveries

Methane Hydrates



Estimated at twice total fossil fuels

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Scope

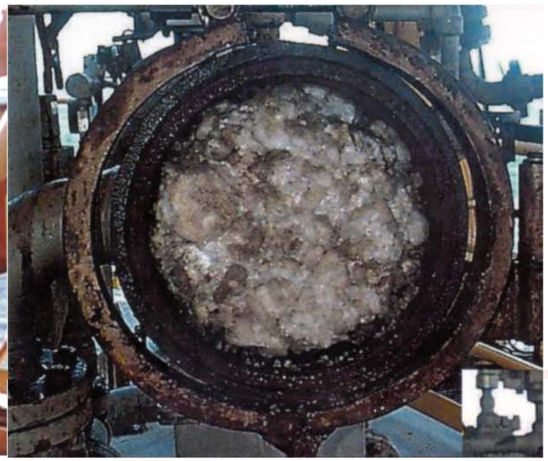
- Why hydrates can be dangerous
- Techniques for avoiding gas hydrate problems
- Hydrate safety margin monitoring
- Hydrate early detection system
- Kinetic hydrate inhibitors
- Conventional testing techniques for KHIs
- New testing techniques
- KHI: challenges and opportunities
- Conclusions

Why Hydrates Can be Dangerous

- Hydrate formation can block pipelines, wellbore/tubing
- Preventing production and/or normal operation
- Prevent access to wellbore

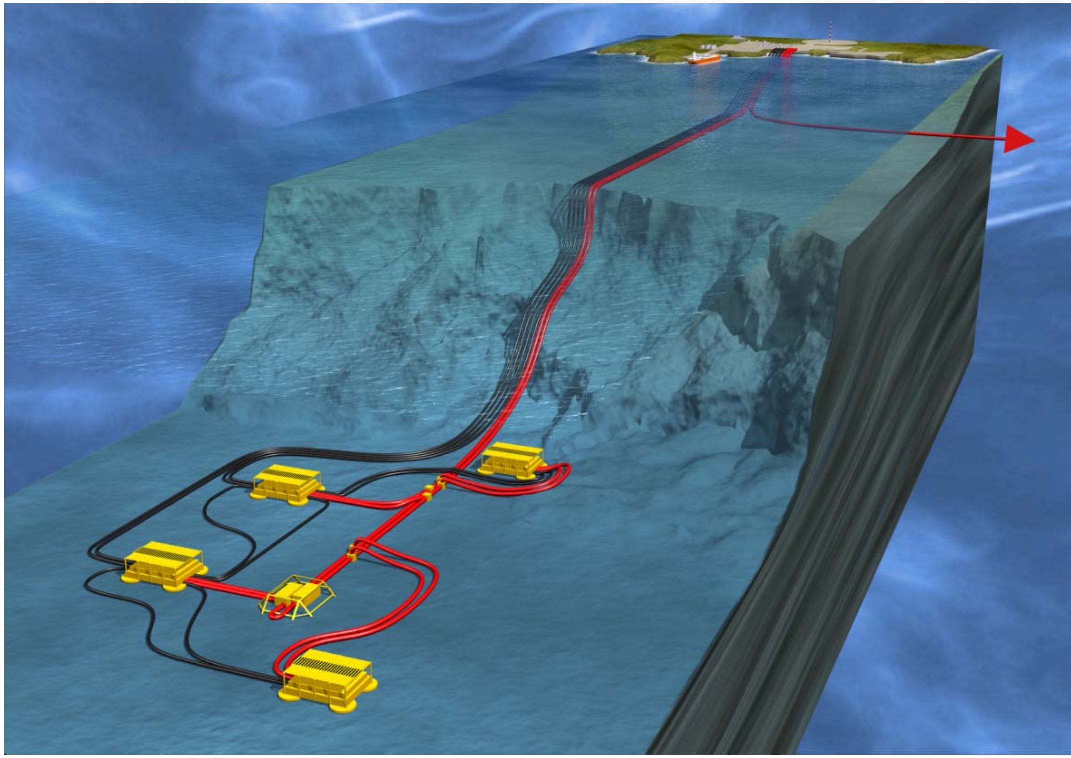
- Therefore, a hydrate blockage should avoided/removed
- There are various options associated with respect to avoiding/removing hydrate blockages

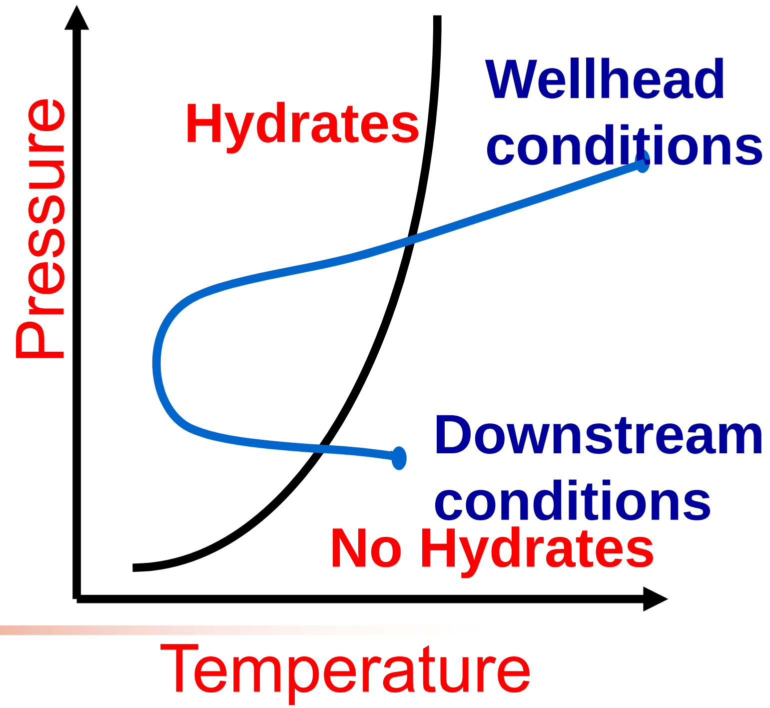
- There are serious risks associated with techniques used for removal of a hydrate blockage



Avoiding Hydrate Problems

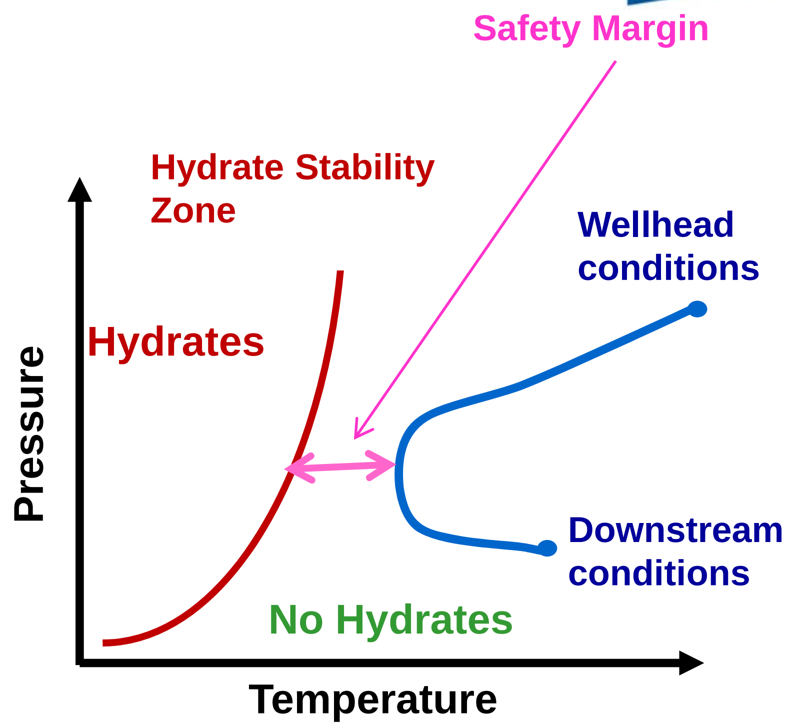
- Water removal (De-Hydration)
- Increasing the system temperature
  - *Insulation*
  - *Heating*
- Reducing the system pressure
- Injection of thermodynamic inhibitors
  - *Methanol, ethanol, glycols*
- Using Low Dosage Hydrate Inhibitors
  - *Kinetic hydrate inhibitors (KHI)*
  - *Anti-Agglomerants (AA)*
- Various combinations of the above
- Cold Flow





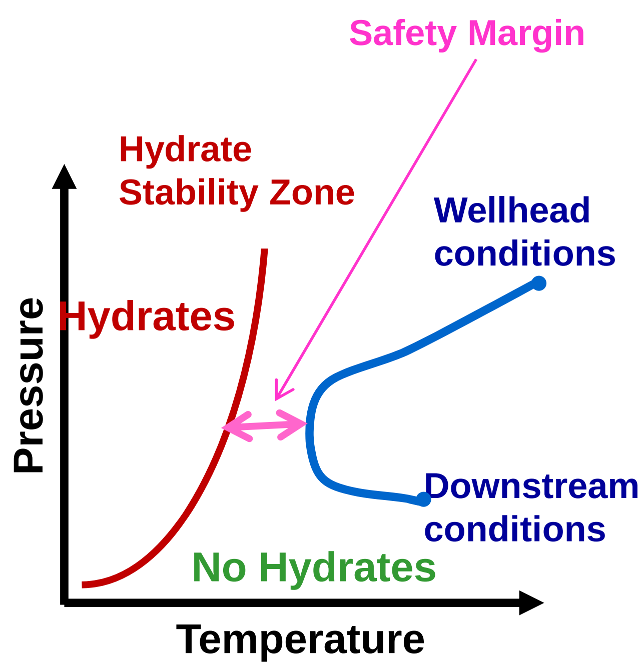
Hydrate Safety Margin Monitoring & Early Detection System

- Methods for determining the hydrate safety margin (HSM) of pipeline fluids
  - *Determining chemical concentrations*
  - *Ensuring adequate inhibition*
  - *Optimising inhibitor injection practices*
- Detecting early signs of hydrate formation
- Ultimately to develop online hydrate monitoring and warning systems



Hydrate Safety Margin: Requirements

- Hydrate Stability Zone
  - *Composition of hydrocarbon phase (normally determined from PVT analysis)*
  - *Hydrate inhibition characteristics of the aqueous phase (composition in most cases)*
    - *Salt*
    - *Chemical hydrate inhibitors (alcohols, Glycols, LDHI)*
- Pressure and temperature profile and/or the worst operation conditions
  - *Computer simulation and/or P & T sensors*



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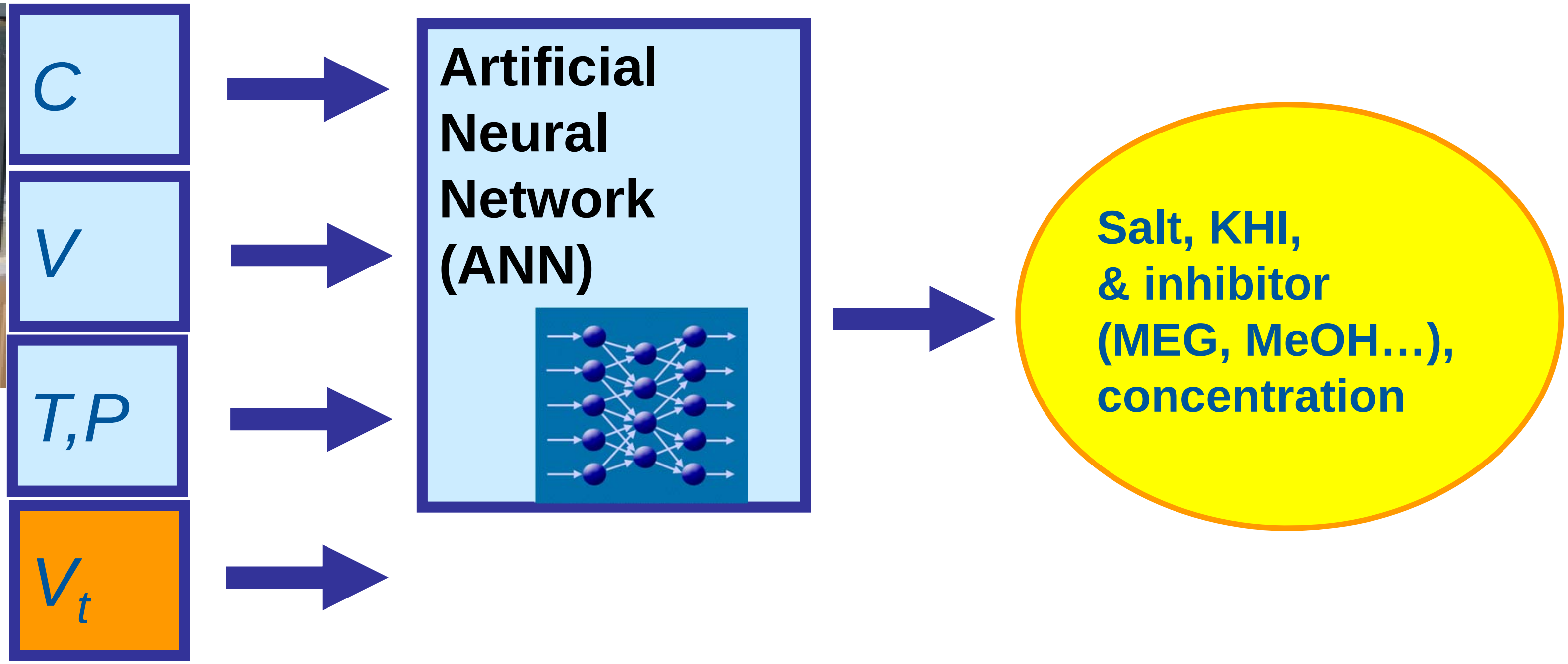
Determining Inhibitor Concentration

Produced water sample analyser



- Measuring electrical conductivity (C) and acoustic velocity (V) in the produced water
- Temperature and pressure are also measured to account for their effect
- The measured parameters are fed into an ANN system which in turn gives salt, KHI and organic inhibitor concentrations

Hydrate Safety Margin Monitoring

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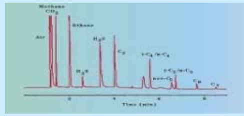
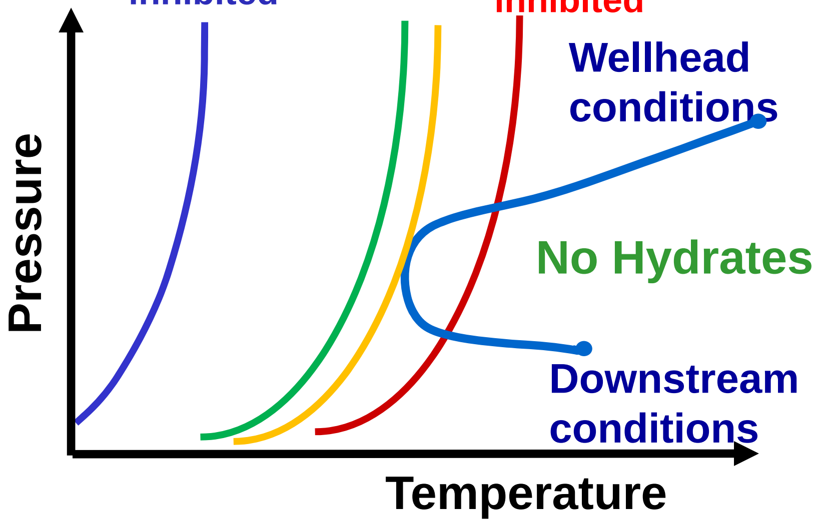
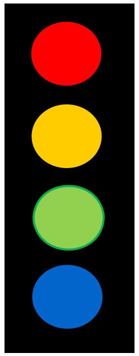


Hydrocarbon composition

Aqueous phase composition
%MEG, %Salt, %MeOH, %KHI

Hydrate model / Correlation





Hydrate risk
Low safety margin
Safe/optimised
Over inhibited

- Knowing the hydrocarbon composition the hydrate stability zone can be determined
- Superimposing the operating conditions, safety margin is determined
- Alternative option for conditions where there is no free water sample

Trials of Safety Margin Monitoring Techniques

- High concentration of MEG by Statoil (Trondheim , Norway)
- KHI systems by Dolphin Energy (Total) in Qatar[1]
- MeOH + salt systems by Petronas in their FPSO lab (Mauritania)
- MEG + salt systems by NIGC (South Pars Gas Complex (SPGC) Field)[2]
- Methanol + salt, Total, Alwyn, North Sea[3]
- Methanol + salt, Woodgroup (Triton FPSO) and Shell (Shearwater) North Sea
- Salt + Inhibitor, ConocoPhillips, North Sea
- Salt + MEG, Petronas (Turkmenistan) and Cameron (Pilot Plant, University of Manchester)
- KHI systems, Champion Technologies
- Salt + Methanol, NUGGETS, North Sea[4]

1. Lavallie, O., et al., *Successful Field Application of an Inhibitor Concentration Detection System in Optimising the Kinetic Hydrate Inhibitor (KHI) Injection Rates and Reducing the Risks Associated with Hydrate Blockage*, IPTC 13765, International Petroleum Technology Conference held in Doha, Qatar, 7–9 Dec 2009.
2. Bonyad, H., et al., *Field Evaluation of A Hydrate Inhibition Monitoring System*. Presented at the 10th Offshore Mediterranean Conference (OMC), Ravenna, Italy, 23-25 Mar 2011.
3. Macpherson, C., et al., *Successful Deployment of a Novel Hydrate Inhibition Monitoring System in a North Sea Gas Field.* Presented at the 23rd International Oil Field Chemistry Symposium, 18 – 21. Mar 2012, Geilo, Norway.
4. Saha, P., Parsa, A. Abolarin, J. "NUGGETS Gas Field - Pushing the Operational Barriers", SPE 166596, at the SPE Offshore Europe Oil and Gas Conference and Exhibition held in Aberdeen, UK, 3–6 September 2013.

Hydrate Inhibitor Monitoring System in a North Sea Gas Field

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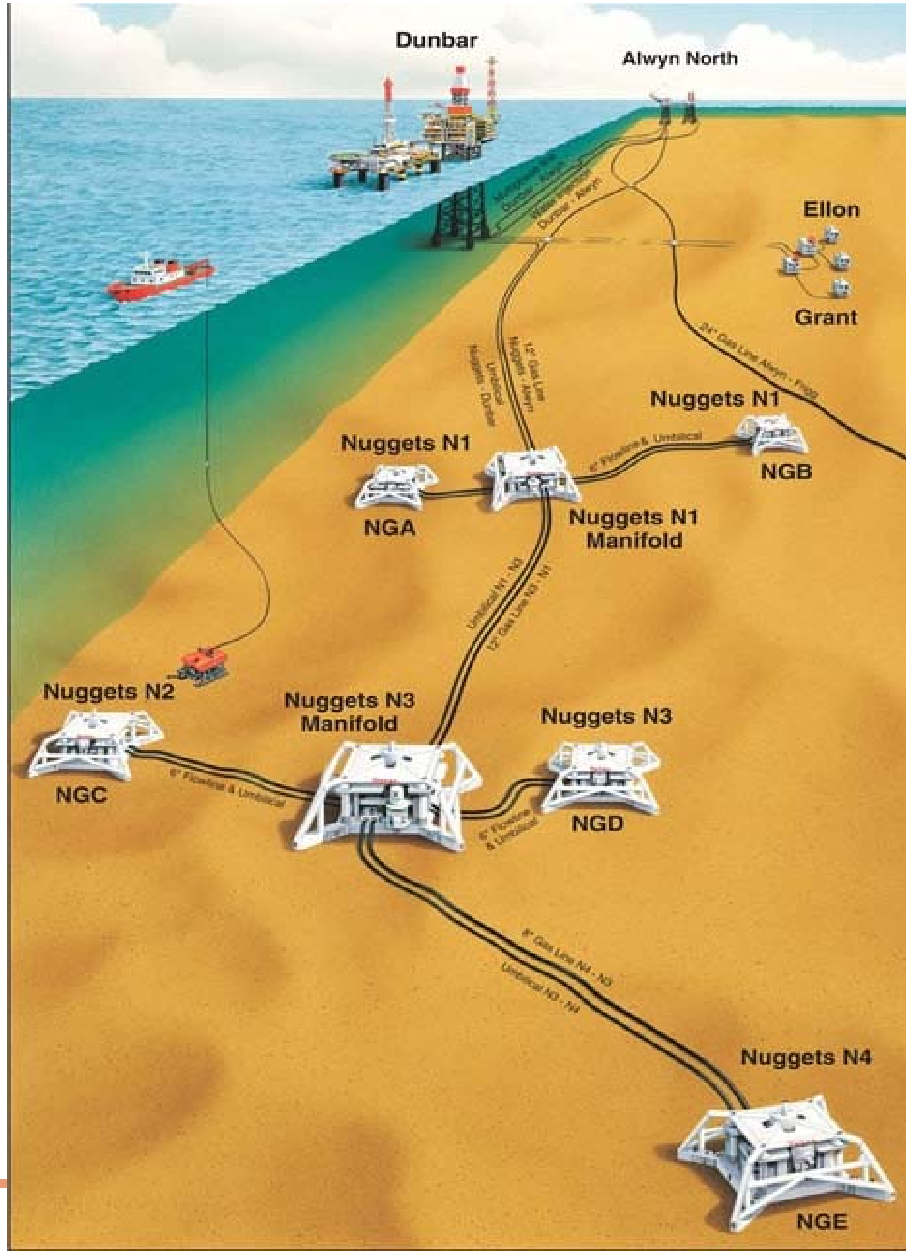
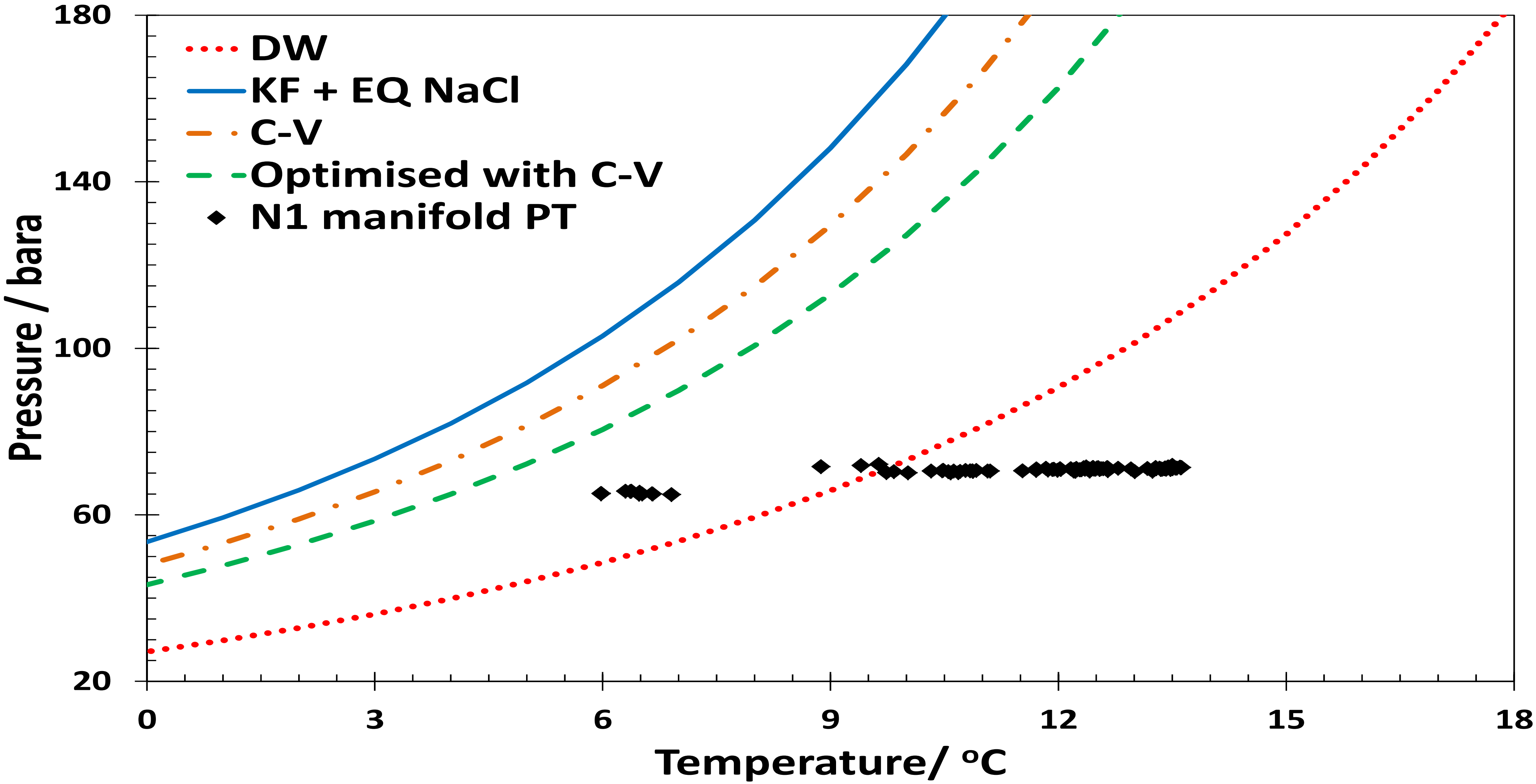
- **Location**
- 4 Gas bearing Eocene Structures
- 40 - 70 Km tie-back
- **Reservoir Characteristics**
- Frigg Sandstone
- Φ=30%, k=2000 - 4000mD; $K_v/K_h \approx 1$
- Reservoir Pressure =155 bara
- Temperature = 57 °C
- C_1 = 98%
- CGR = 2.1 E-6 Sm^3/Sm^3
- Strong aquifer influx



Hydrate Phase Boundary



- Methanol injection was reduced to less than 5 wt% from designed 28 wt%
- Savings in the order of millions of GBP per year

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Minimising Methanol Injection

Nuggets Gas Field – Pushing the Operational Barriers (SPE 166596)

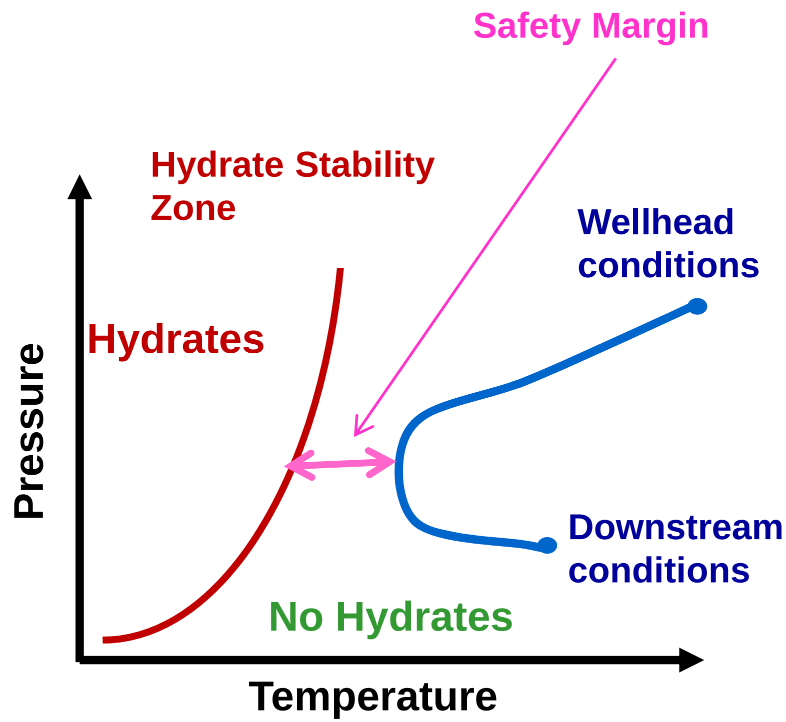
- In 2010 the water production rate reached its maximum
- On the other hand methanol was causing product contamination
- Methanol injection was reduced to practically zero
  - *Methanol is being used only as a carrier fluid for corrosion inhibitor*
- The system was operated inside the Hydrate Stability Zone
  - *Hydrate Slurry Transport*
  - *Salinity increase was used as a measure for monitoring hydrate formation and concentration of hydrates in the slurry*

Results

- Nuggets field life has been extended by three years with ***an incremental production of nearly 3 million BOE to date***
- Steady production operations below nominal turndown and operating within hydrate zone
- Significant reduction of Methanol usage
- Field life has been extended by 3 years with the possibility of further prospects being tied-in to the existing facilities
- 2% increase in Recovery Factor
- Extra income of tens of millions GBP per year

Summary/Conclusions

- A robust and quick technique based on measuring electrical conductivity and acoustic velocity has been developed for determining concentration of salts and hydrate inhibitors in an aqueous phase
- The technique has been tested extensively (in various laboratories and fields)
- A hydrates safety margin monitoring technique based on measuring the amount of water in the gas phase has been developed

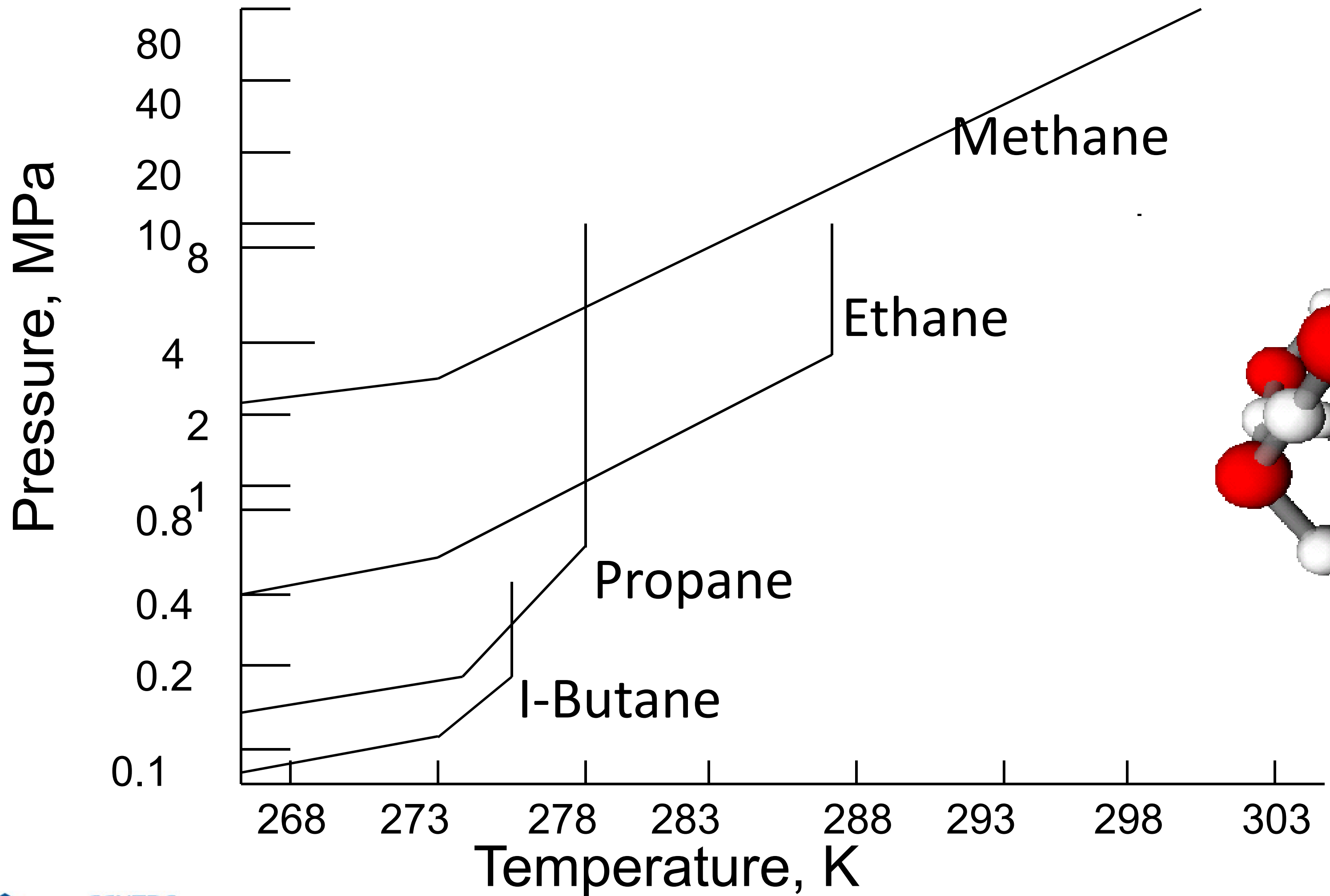


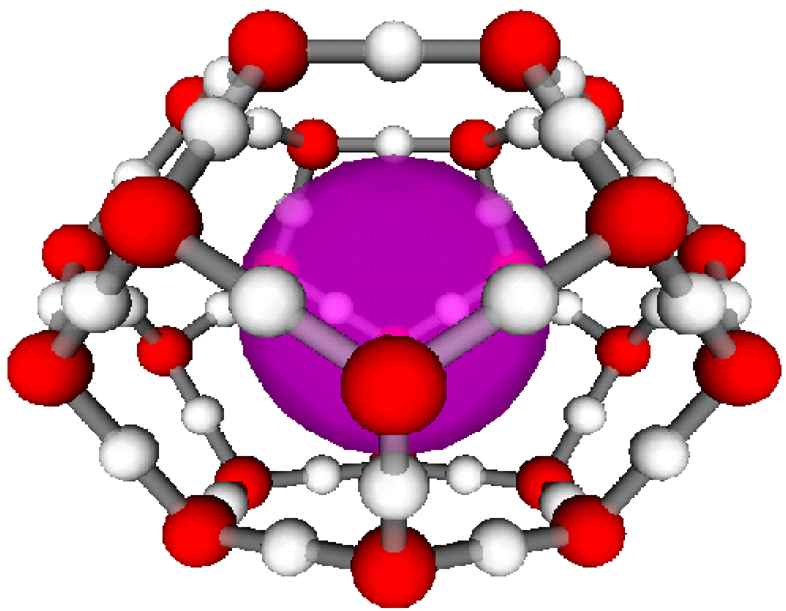
Hydrate Early Detection System

- It is believed initial hydrate formation does not result in pipeline blockage in many systems
- Therefore, detecting the signs of initial hydrate formation could provide an early warning system
- Hydrates prefer large and round molecules (e.g., C_3 and i-C_4 for sII hydrates) in their structures
- Hydrate formation results in a reduction in the concentration of large and round molecules in the gas phase
- Can we use this property as an early detection technique against background compositional changes?

Detecting Early Signs of Hydrate Formation

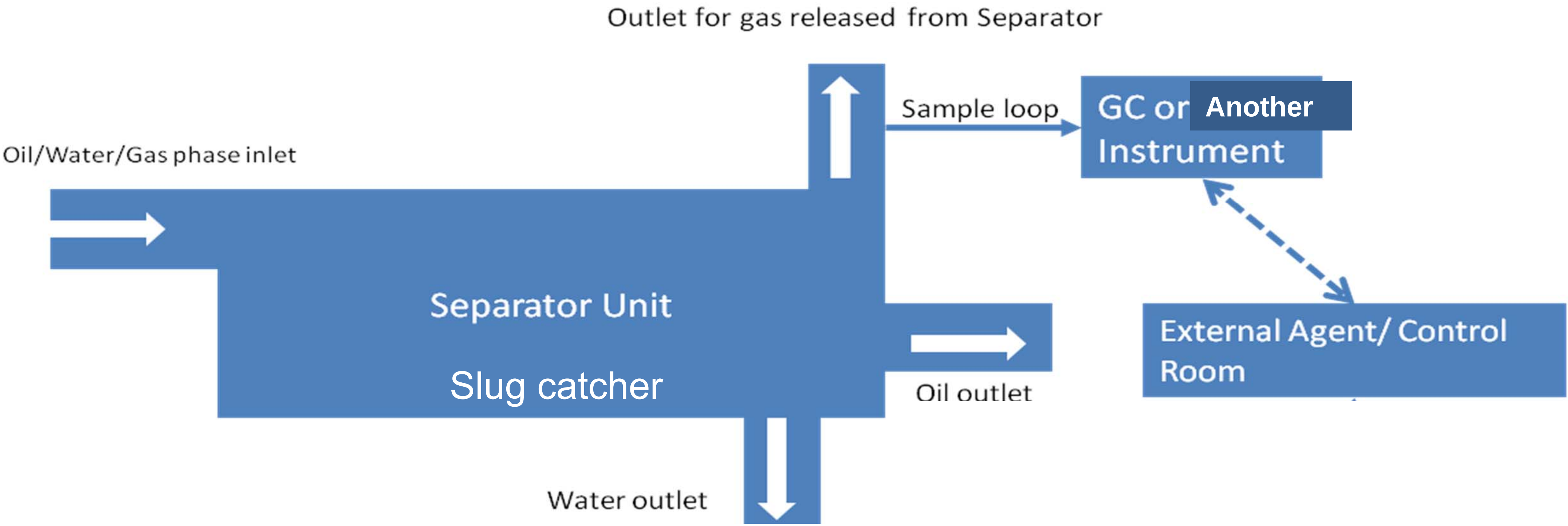
- Hydrates prefer large and round molecules (e.g., C_3 and i-C_4 in sII hydrates) in their structures





$5^{12}6^4$

Potential Implementation Configuration



Hydrate formation results in a reduction in the concentration of large and round molecules in the gas phase

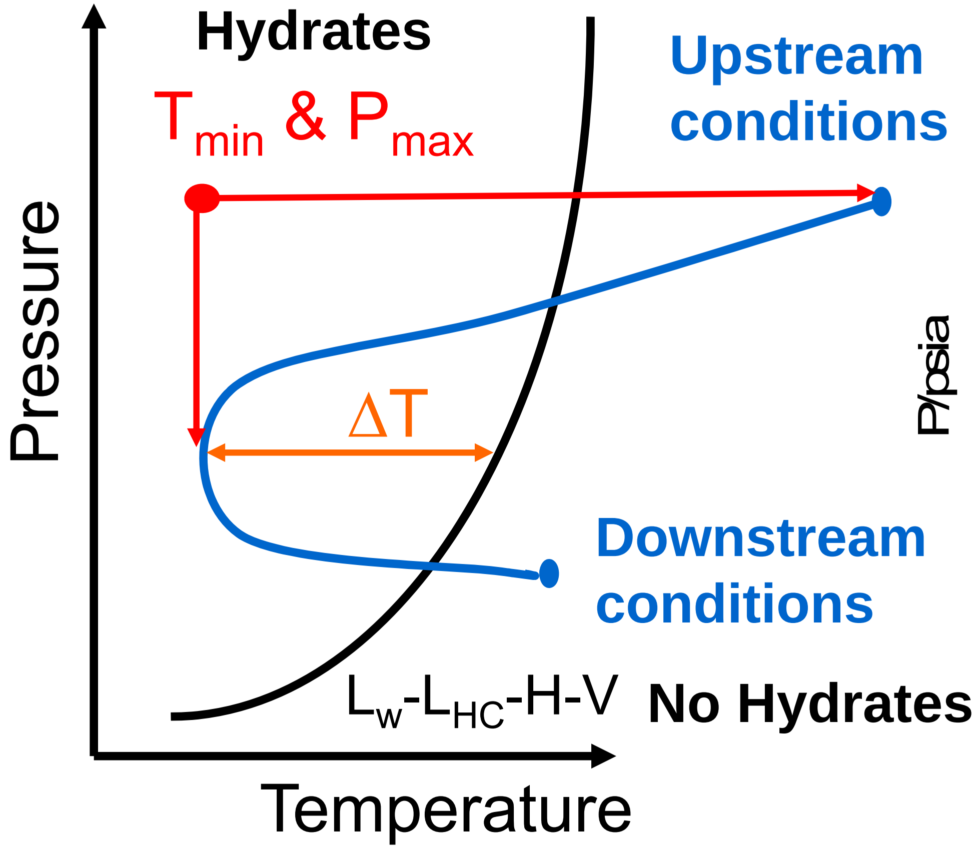
Field Demonstration/Trial

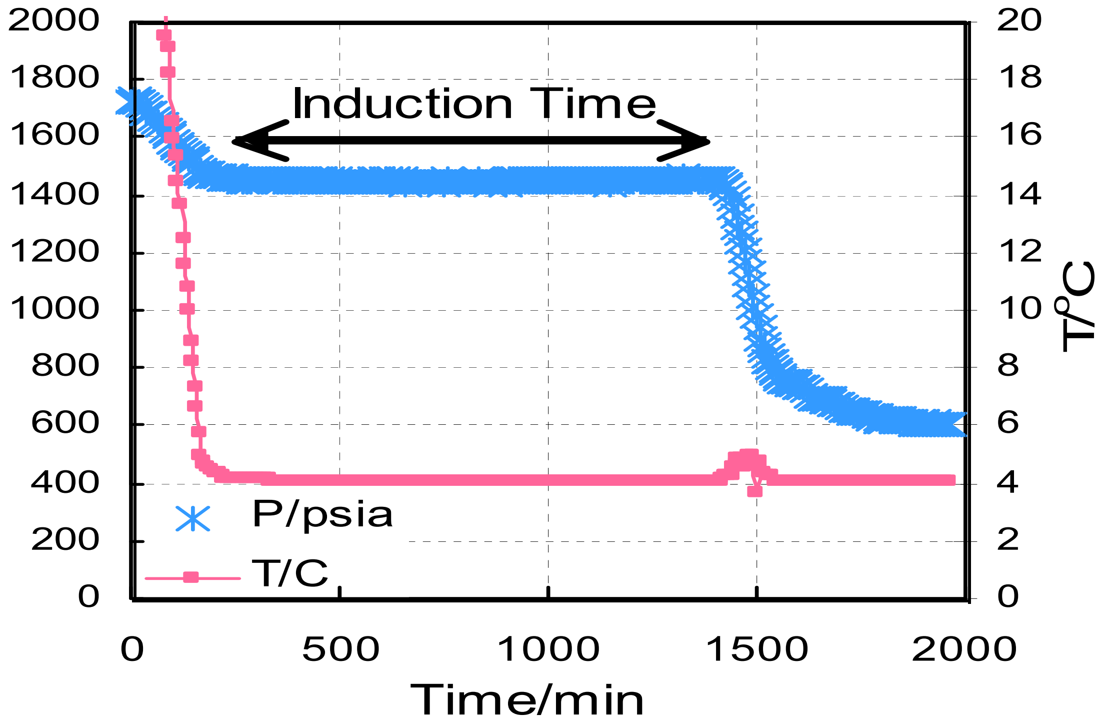
- Mature gas field
- Very high gas to condensate ratios
- High water cut, hence switched to AA for Hydrate Blockage Control
- Online Gas Chromatograph was installed to see if hydrate formation can be detected
- The field trail was successful, detecting early signs of hydrate formation
- Hydrates were forming mainly at night times
- The results could be used to optimise AA injection
- A paper is being prepared and will be presented at the 8th International Conference on Gas Hydrates in July 2014

Summary/Conclusions

- A technique for detecting early signs of hydrate formation from monitoring changes in the gas composition has been developed and extensively tested in the lab
- Hydrate formation could be detected by monitoring the gas phase composition
- A field trial of the technique was successful
- If you had a near miss, it would be good to test the technique against gas compositional/volume data
- Integration of hydrate safety margin monitoring and early detection could provide a powerful tool for minimising inhibitor injection rate and improving the reliability of hydrate prevention techniques

Avoiding Hydrate Problems-Kinetic Hydrate Inhibitor





Test Conditions: Minimum Temperature & Maximum Pressure!!!

Induction time should be longer than the fluid residence time!

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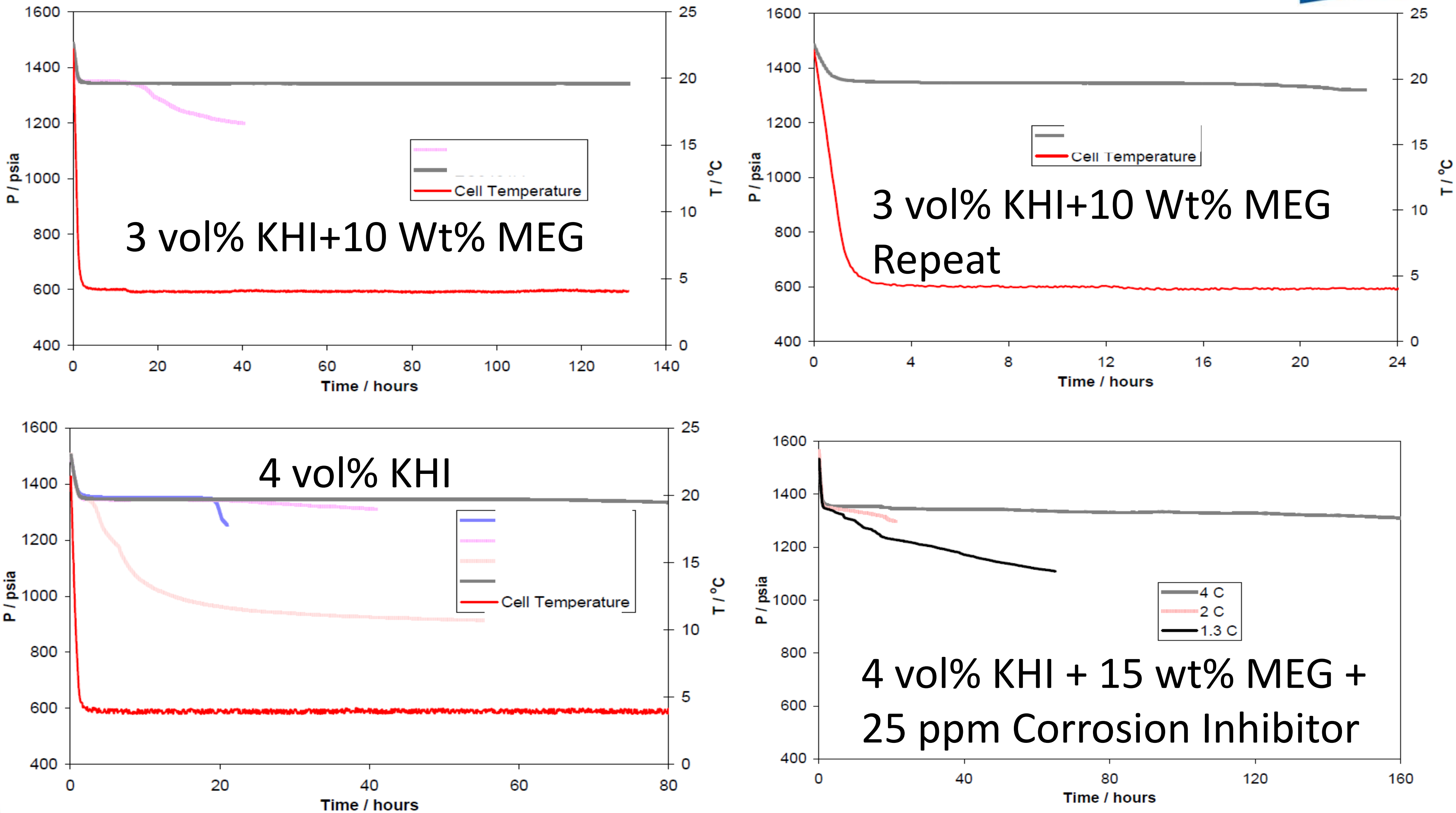
KHI Performance Testing



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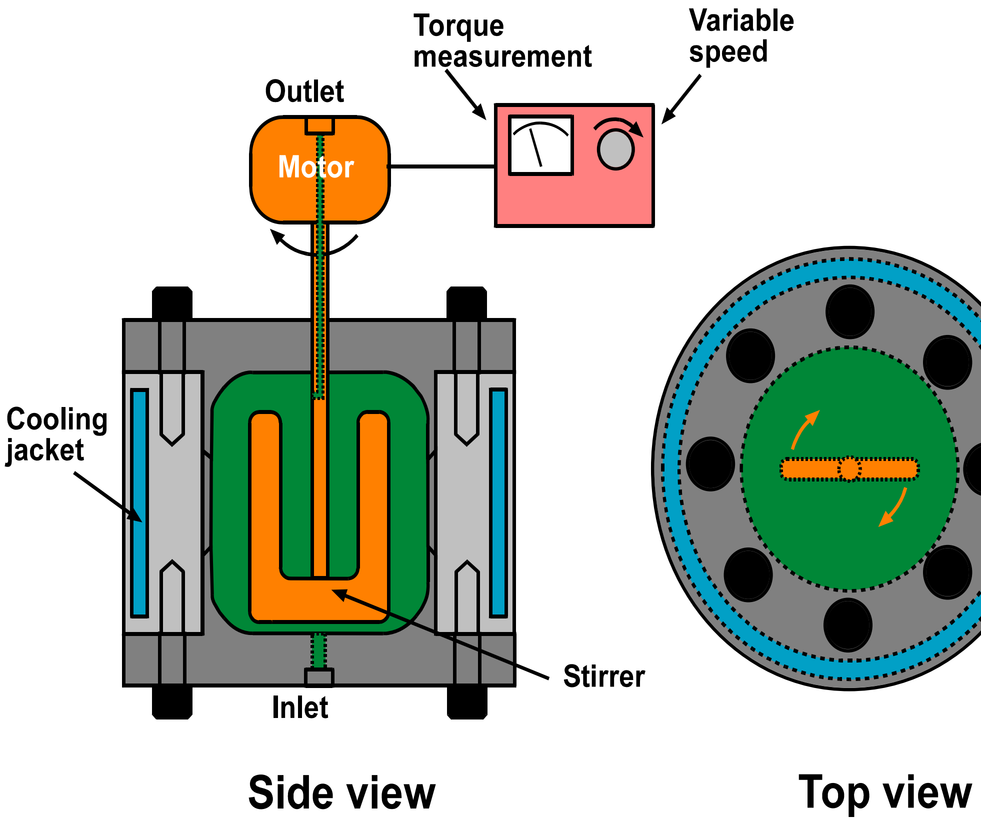
KHIs: New Evaluation Method

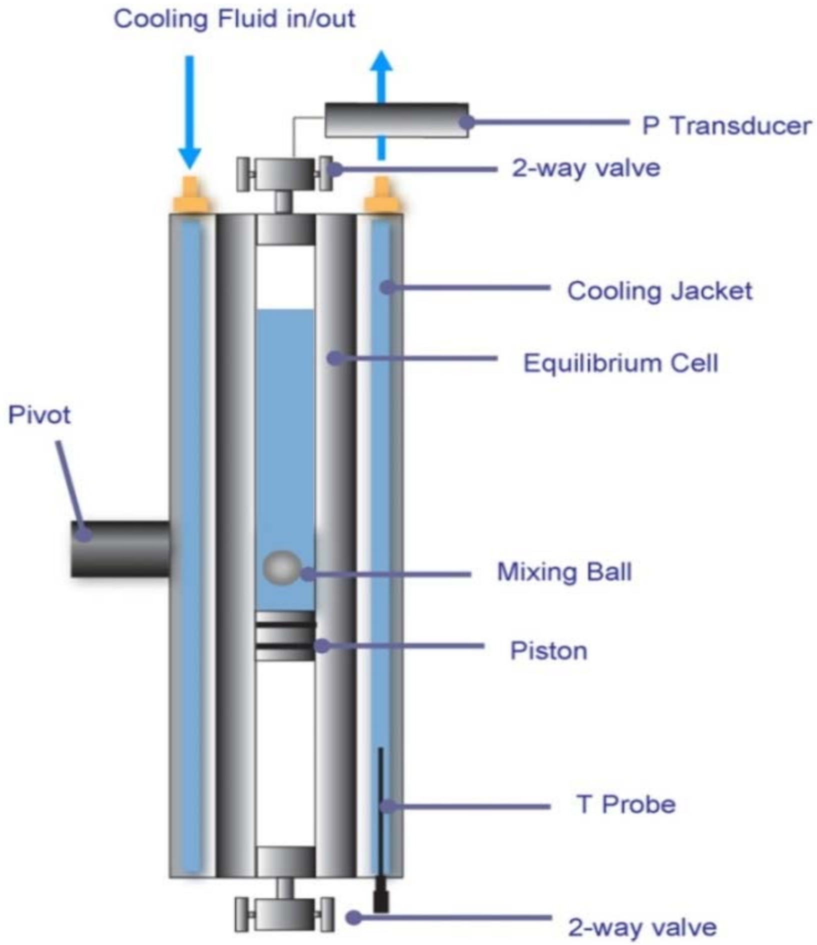
- Problems associated with induction-time based approach
  - *Lack of repeatability, suitability questions in shut-in conditions, hydrate formation at the top of the pipeline, time requirements*
  - *Lack of predictability*
  - *Poor operator confidence: hindering KHI adoption*

- Benefits of the new approach
  - *Faster KHI evaluation process*
  - *Providing robust, repeatable and transferable KHI data*
  - *Increasing operator confidence in KHI performance*
  - *Improving our understanding of KHI inhibition mechanisms*

- New 'CGI (Crystal Growth Inhibition)' method developed 2009-12 at Heriot-Watt University

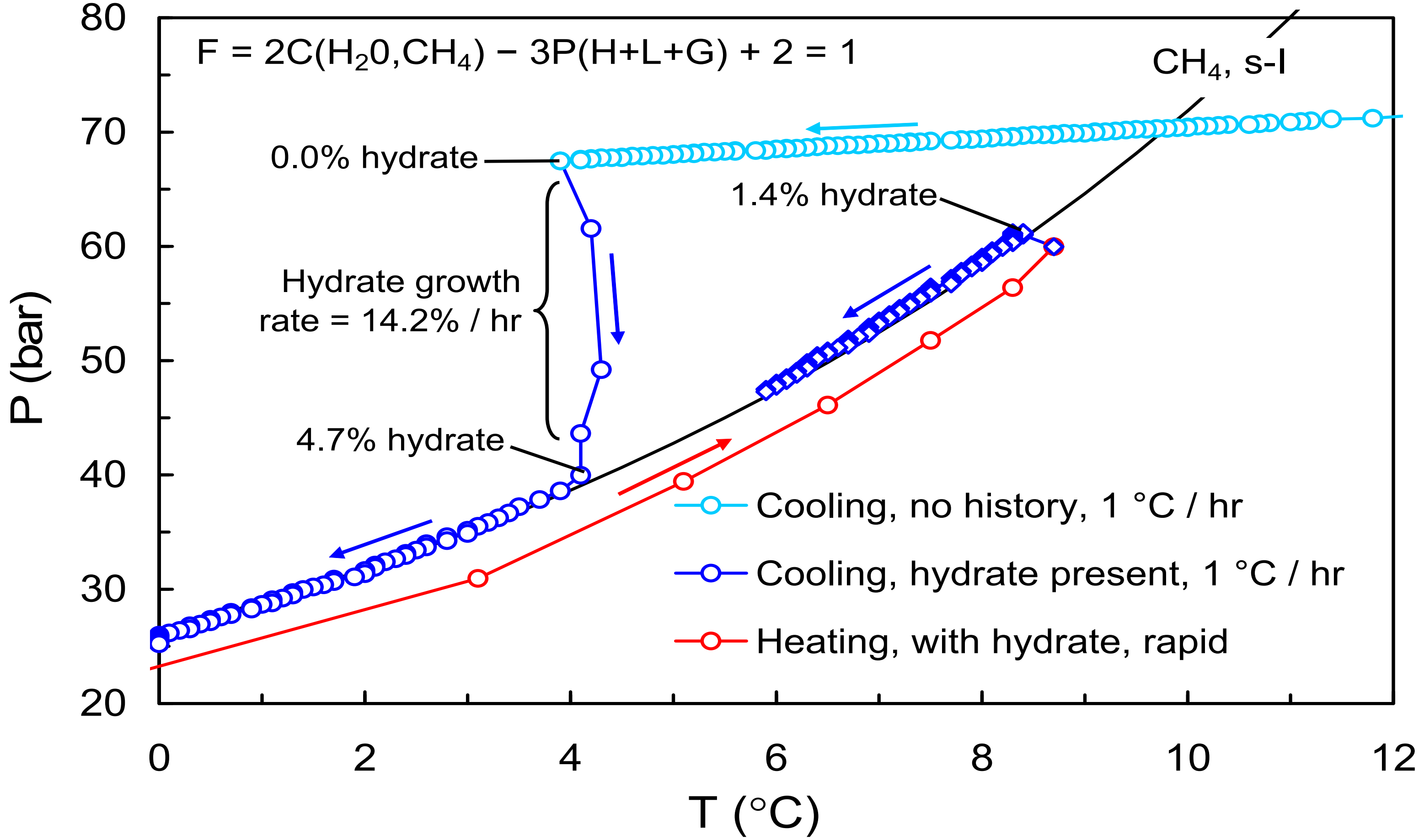
KHIs: Standard Lab Equipment





High pressure autoclaves or rocking cells – as standard for hydrate studies – can be used for KHI CGI and t_i evaluation studies

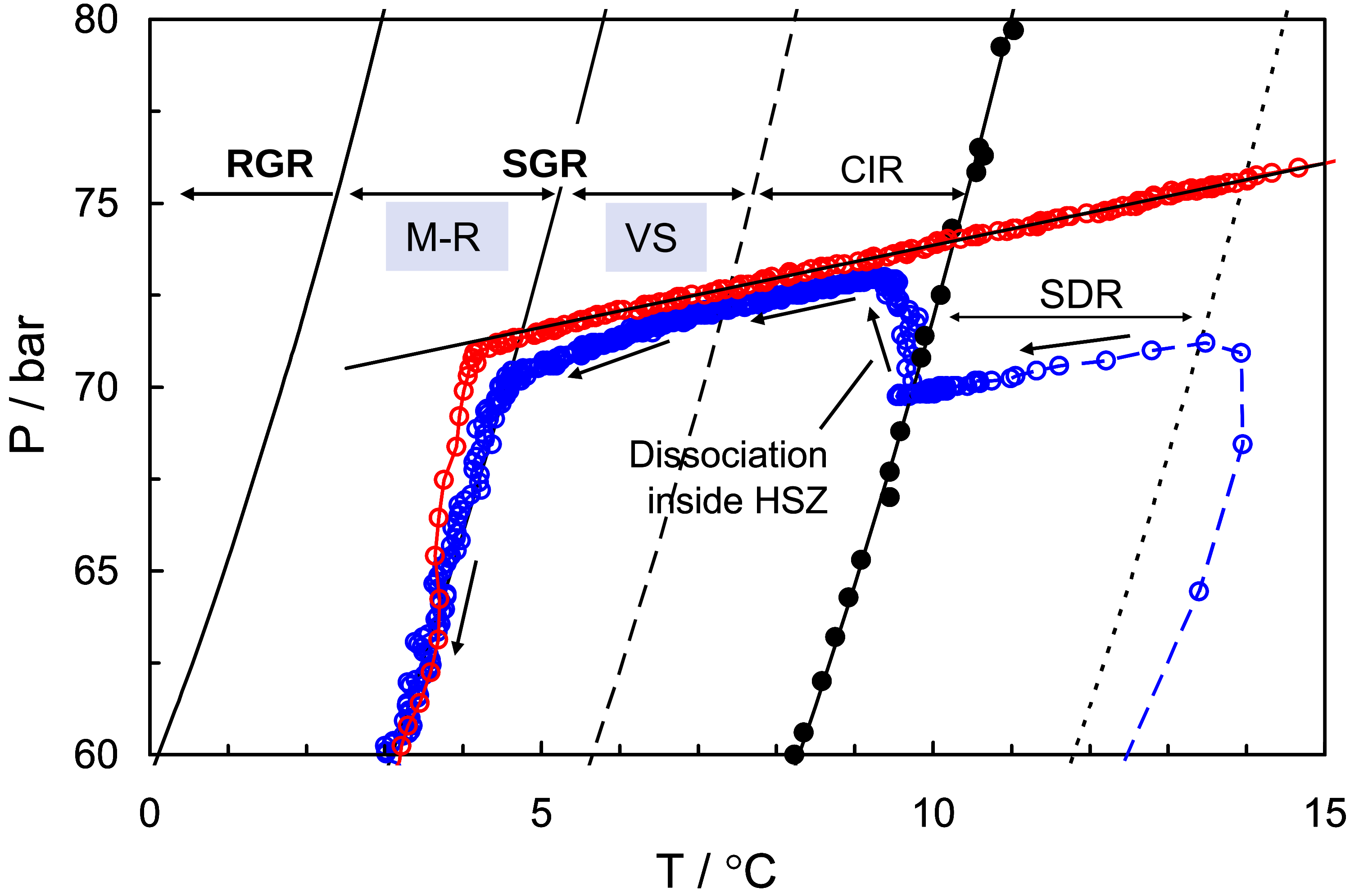
KHIs: CGI Method Basics



With no KHI, if hydrate is present, growth / dissociation occurs rapidly in response to temperature changes as expected

Example CGI cooling and heating data for water with methane (no KHI)

KHIs: New CGI Approach Test Procedures



Determination of CGI regions for 0.25 mass% PVCap with methane

SDR = Slow Dissociation Region
CIR = Complete Inhibition Region
SGR = Slow Growth Rate region
RGR = Rapid Growth Region

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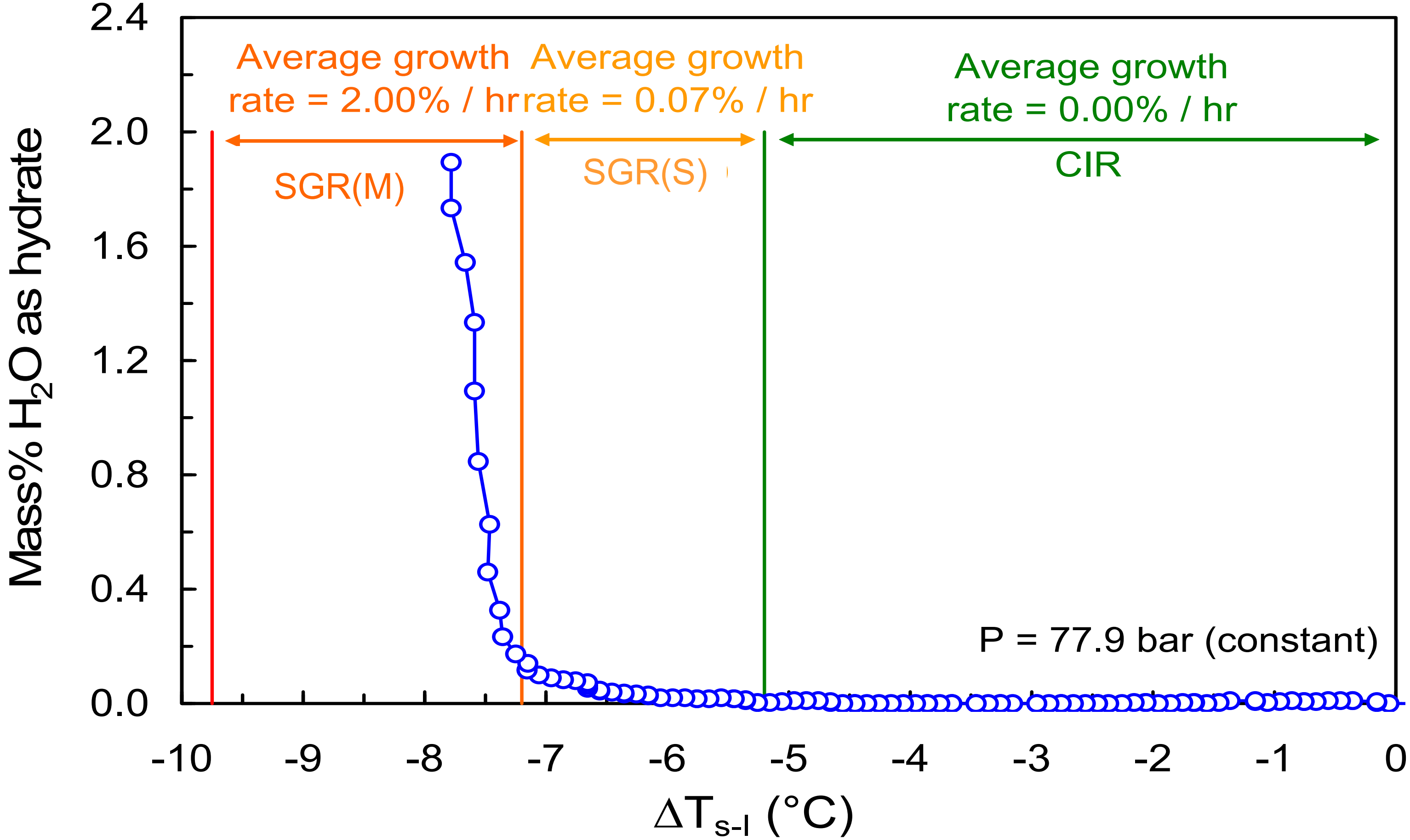
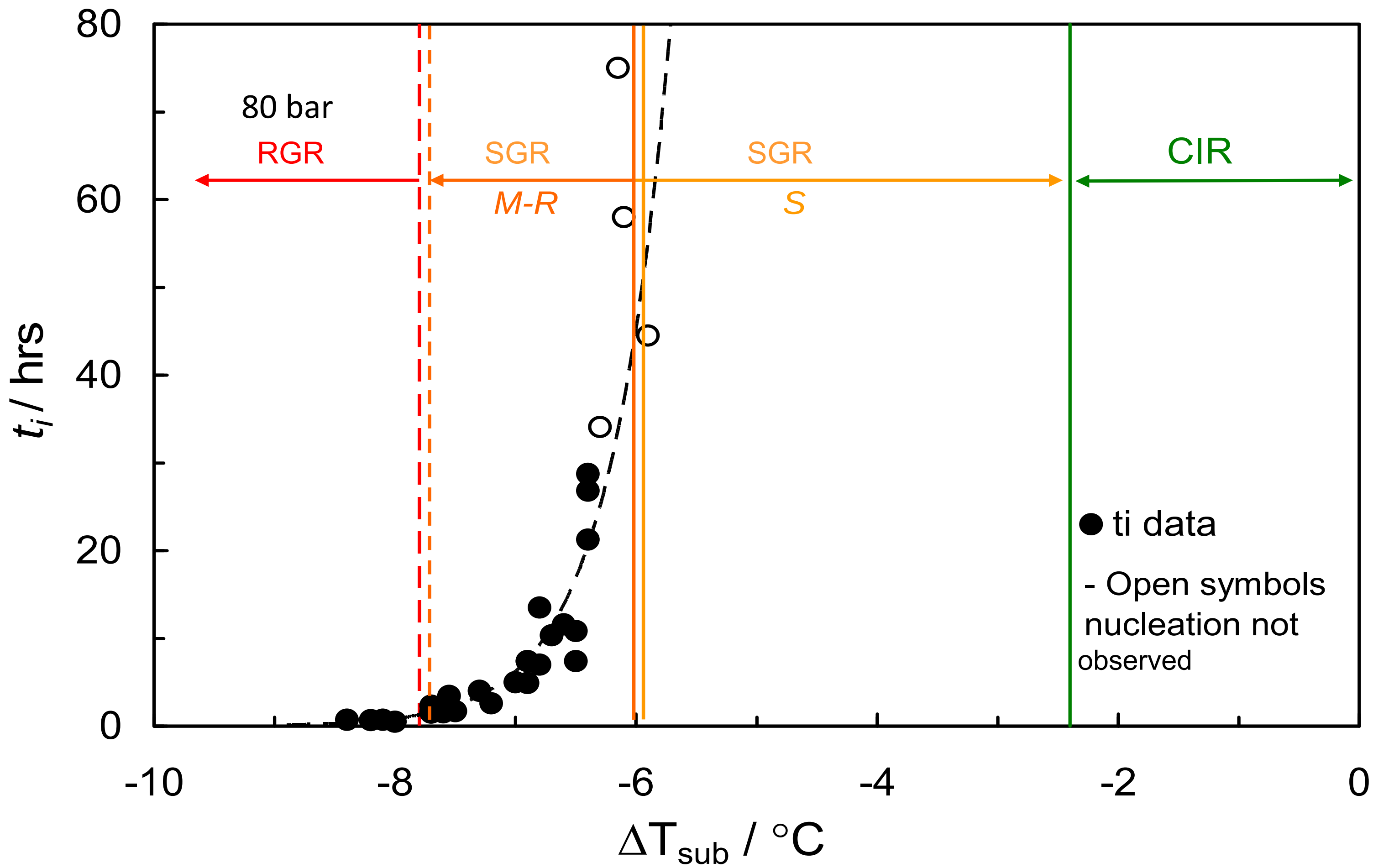
Amount of Hydrates Formed vs Subcooling



CGI Results are identical whether constant pressure or constant volume approaches are used

Example CGI cooling run at constant pressure for 0.5 mass% PVCap aqueous with methane. Points are every 5 minutes

KHIs: CGI and t_i



Induction times closely linked to CGI regions

Explains 'scatter' over short subcooling range & why t_i impossible to measure at low subcoolings….

Measured CGI regions and t_i data vs. subcooling for 0.5 mass% PVCap aqueous with methane

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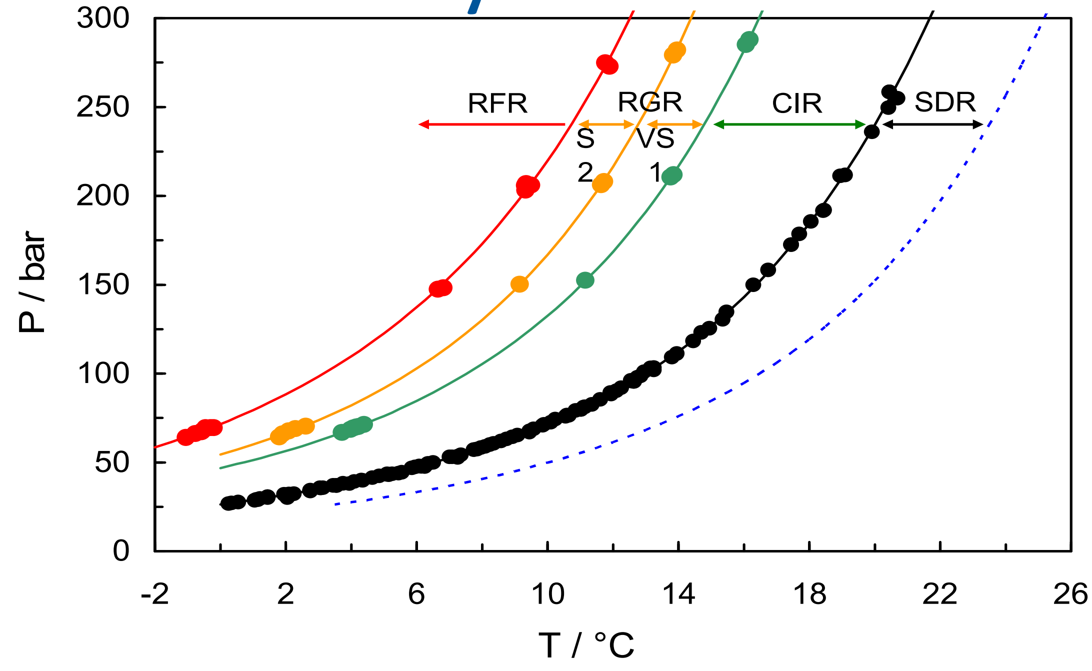
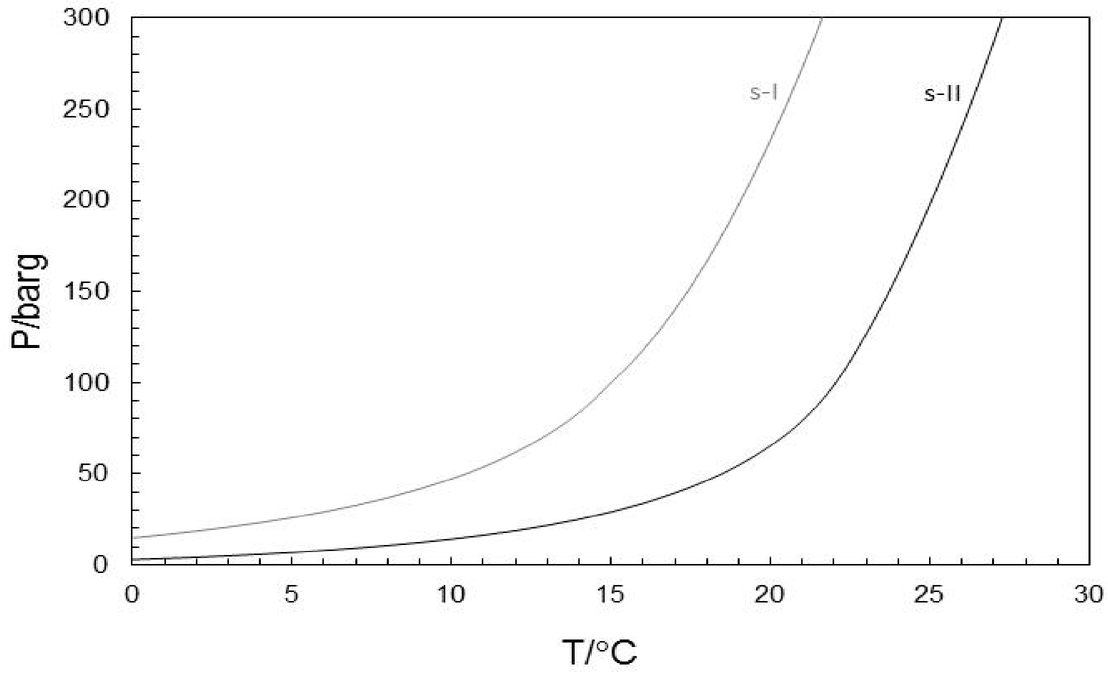
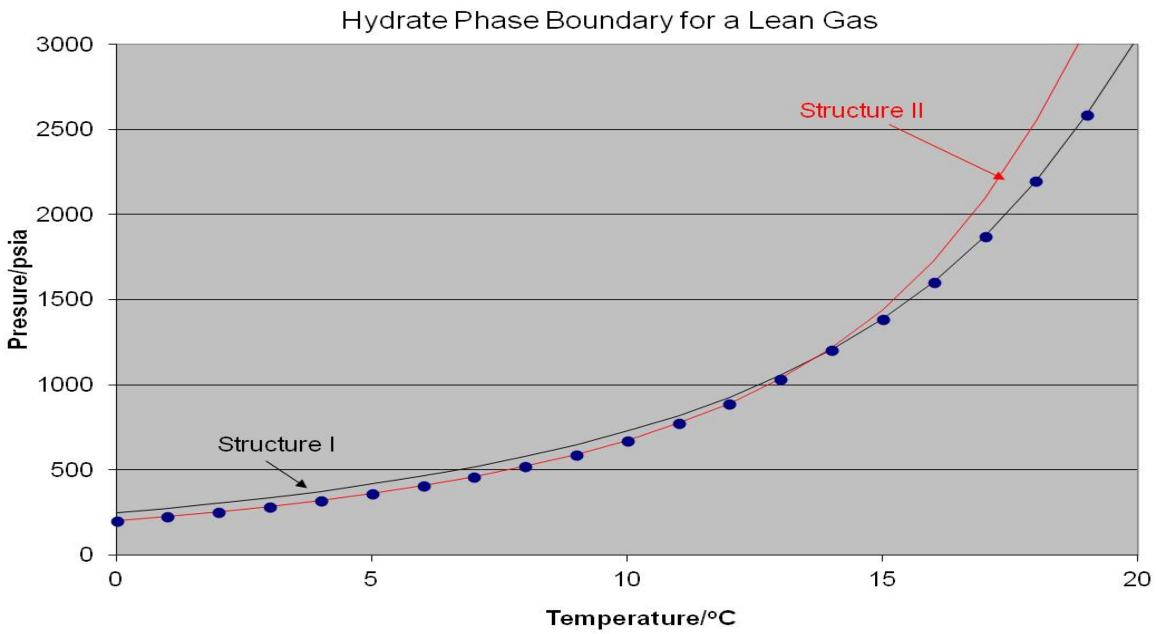
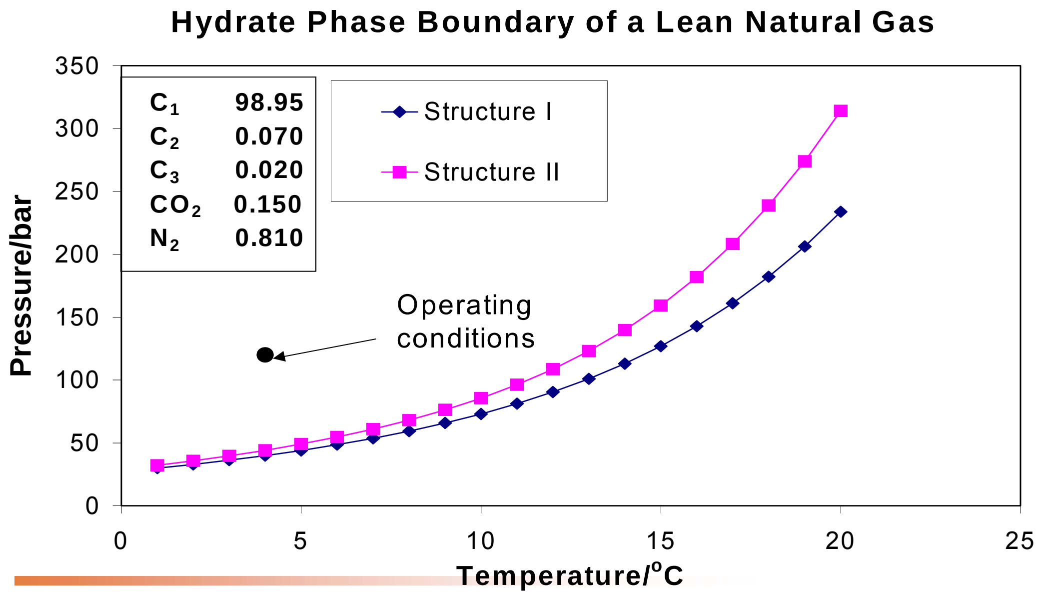
Role of Hydrate Structure

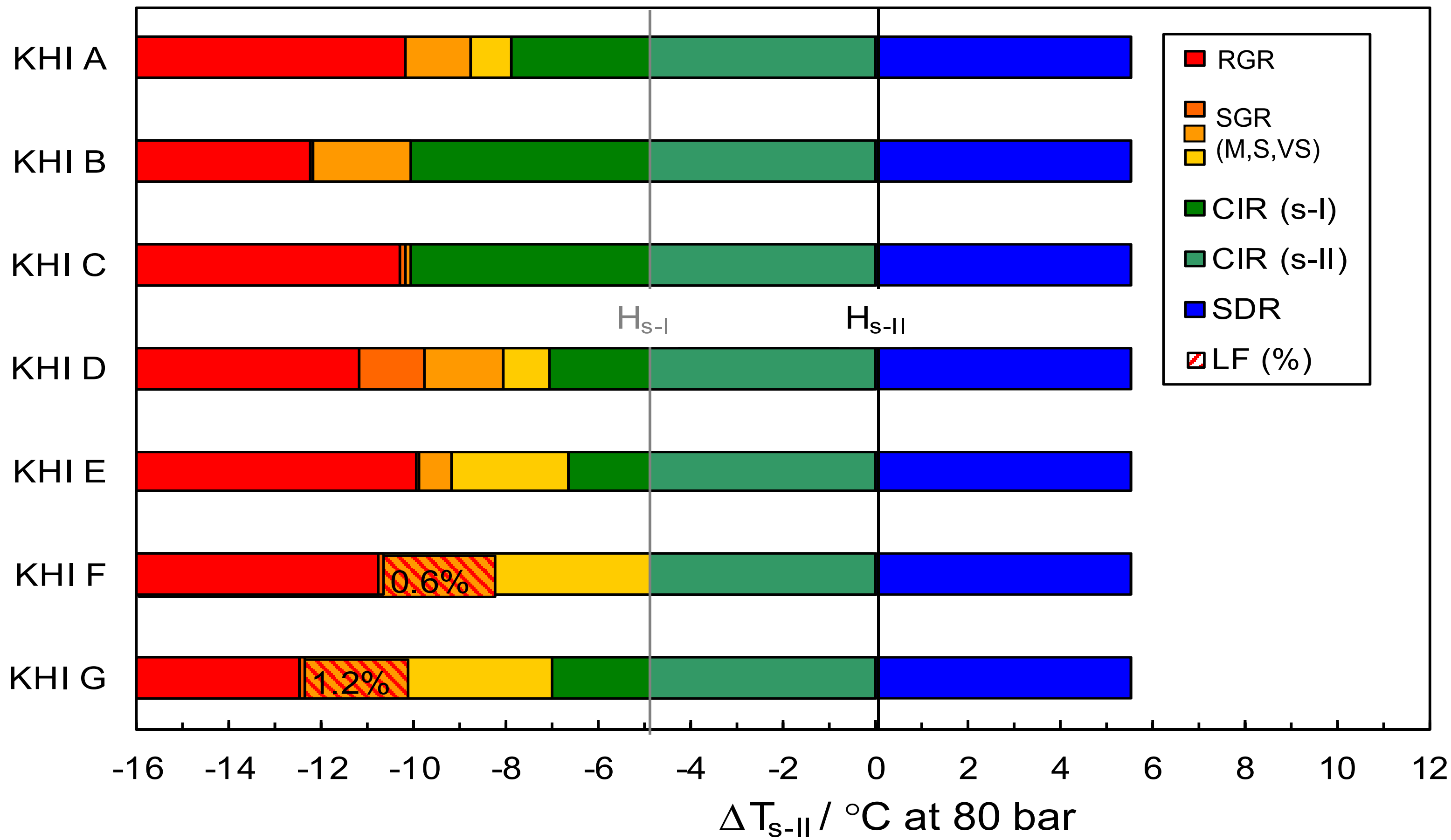








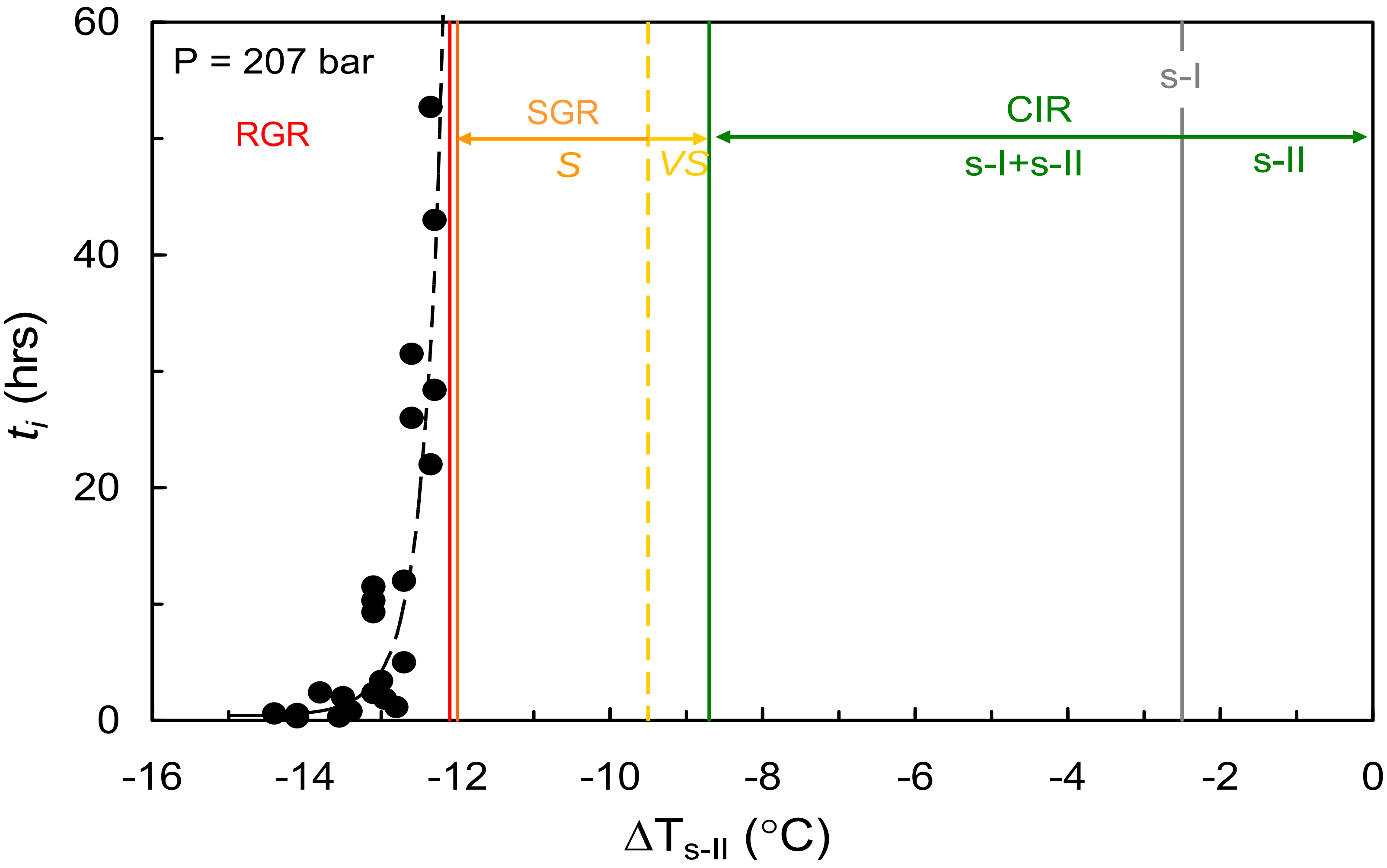
KHIs: Evaluation using CGI method



CGI regions can be used to robustly compare relative KHI hydrate inhibition performance at pipeline conditions

Measured CGI regions for a range of commercial KHIs with a synthetic natural gas and real field condensate (real field development evaluation)

KHIs: CGI and t_i



Induction times closely linked to CGI regions

Explains 'scatter' over short subcooling range & why t_i impossible to measure at low subcoolings….

Measured CGI regions and t_i data vs. subcooling for 0.5 mass% PVCap aqueous with standard North Sea natural gas

KHI Testing Techniques: Conclusions

- KHIs provide an effective means to mitigate hydrate problems while offering significant CAPEX/OPEX savings
  - *Being used increasingly and with success in the field*
- Novel crystal growth inhibition (CGI) studies show:
  - *KHIs induce well-defined CGI regions as a function of subcooling ranging from complete inhibition (even dissociation), through severely to moderately reduced growth rates, to final rapid/catastrophic growth as subcooling increases*
  - *Closely related to induction time patterns*
  - *Method provides a means to assess KHIs more rapidly and reliably*
  - *Increased confidence as for worst case scenario (hydrate present)*
  - *Can be used to better understand inhibition mechanisms / effect of other chemicals*

KHIs: Opportunities and Challenges

KHI in Stratified Flow

Past

- KHIs cannot be used under stratified flow, as there would be no KHI in the gas phase, hence hydrate can form from the condensed water at the top of the pipeline
- This can block the pipeline on its own, or hydrates from the top of the pipeline coming into contact with the liquid containing KHI will result in KHI failure in the liquid phase

Now

- We now know that KHIs can act as thermodynamic inhibitor within CIR (Continuous Inhibition Region), so if the system is within CIR hydrate crystals will not result in KHI failure
- In fact tests show that hydrates could melt if they come into contact with aqueous phase containing KHI within CIR

KHIs: Opportunities and Challenges

KHI in Produced Water Processing/Re-Injection

Past

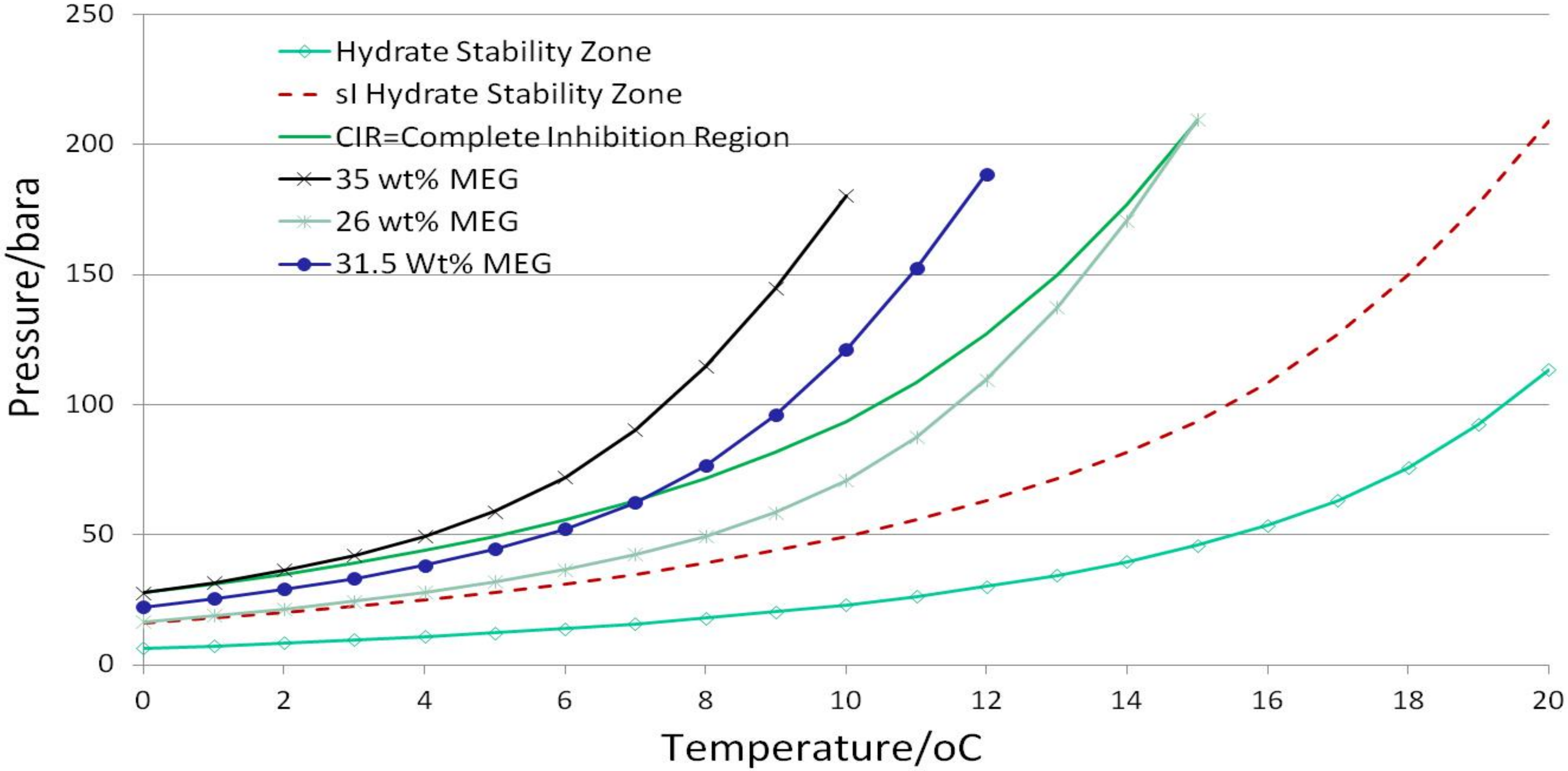
- KHIs are polymers and their cloud point could be around 40 °C
- They can cause problem in pumps inlet strainers in hot environment
- They can cause blockage in produced water re-injection wells

Now

- We can now remove KHIs from produced water by a solvent extraction technique
- The technique is based on adding a solvent to the aqueous phase after 3-phase separator

KHIs: MEG Equivalent

Components	Mole%
Methane	56.14
Ethane	8.26
Propane	3.36
i-Butane	0.56
n-Butane	1.00
i-Pentane	0.40
CO2	6.76
Nitrogen	0.35
n-Pentane	0.34
n-Heptane	0.42
n-Octane	0.53
n-Nonane	0.57
n-Nonane	0.32
n-Decane	0.98



Hydrate stability zone of the above fluid in the presence of condensed water. The green line is the estimated Complete Inhibition Region (CIR) where KHI can provide indefinite inhibition, similar to thermodynamic inhibitors. The results showed that KHI can replace 26-35 wt% MEG, depending on the operating (or worst) conditions.

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KHIs: Opportunities and Challenges

KHI in Produced Water Processing/Re-Injection

Past

- KHI can replace large quantities of MEG (e.g., 20 to 40 wt%)
- This can result in a reduction in MEG regeneration units and/or handling higher water cuts, longer field life, higher recovery factor
- However, due to problems associated with gunking in MEG regeneration units, the full advantages of this combination have not been realised

Now

- We can now remove KHIs from produced water by a solvent extraction technique
- The technique is based on adding a solvent to the aqueous phase after 3-phase separator
- The produced water, free of KHI, can be sent to MEG regeneration units

KHIs: Opportunities and Challenges

KHI in Well Testing

Past

- KHI can replace large quantities of thermodynamic inhibitors (e.g., 20 to 40 wt%)
- This can result in a reduction in the usage of thermodynamic inhibitors, and discharge to the environment
- However, most KHI formulations are regarded as environmentally unacceptable

Now

- We can now remove KHIs from produced water by a solvent extraction technique
- The technique is based on adding a solvent to the aqueous phase after 3-phase separator
- The produced water, free of KHI with much reduced inhibitor concentration, can be discharged to the environment

KHIs: Opportunities and Challenges

Costs and Environmental Issues Associated with KHI

Past

- KHIs are injected in upstream and disposed with produced water
- KHI are expensive and in general environmentally unfriendly
- This, combined with uncertainties in their effectiveness has limited their application

Now

- We can now remove KHIs from produced water by a solvent extraction technique
- The KHI-rich solvent can be removed from the aqueous phase

Conclusions

- Technique for determining hydrate safety margin could minimise inhibitor injection rates, increase reliability, increase field life
- An online system has been developed and ready for field trial
- Early detection systems could play an important role in avoiding gas hydrate blockages and minimising inhibitor injection rates
- New testing techniques are reliable and repeatable
- It is now possible to predict if KHI could be an option for a certain development
- New understandings open new opportunities, e.g., shut-in conditions, re-starts, hydrates at top of pipelines, KHIs can replace large quantities of MEG
- KHI removal eliminates some of PWRI problems and allows combined KHI+MEG allocations
- KHI removal potential could play a major role in future KHI design

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