Advances in Avoiding Gas Hydrate Problems

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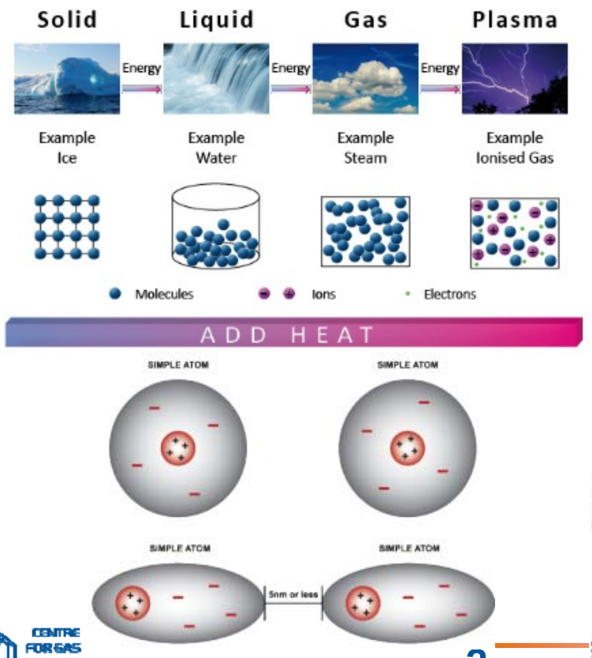
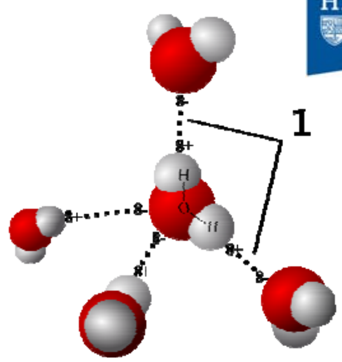
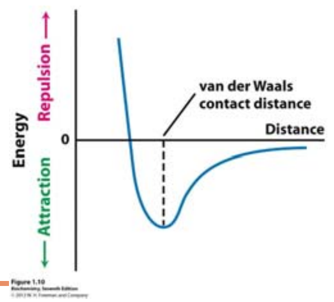
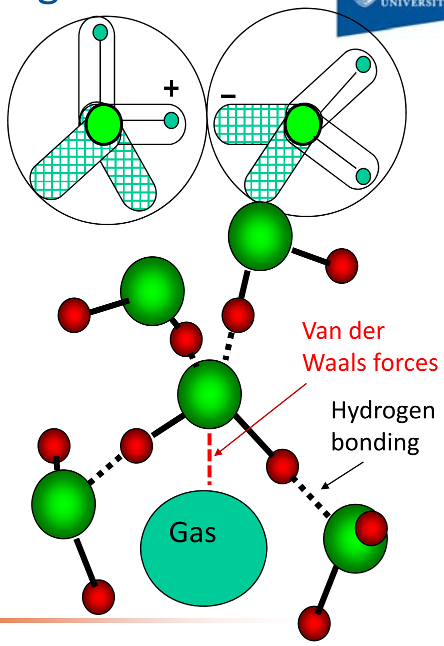






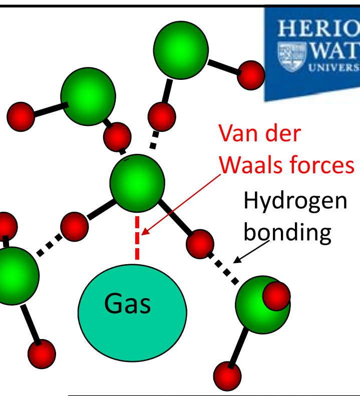
H_2O States, Hydrogen Bonding

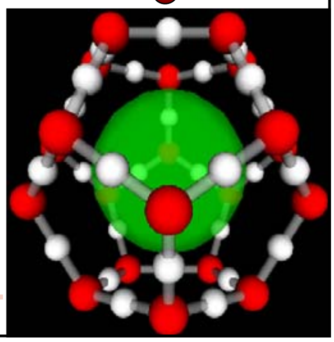
- Gaseous State (water vapour):
  - Molecules are separated, gas will fill the space available
- Liquid State (liquid water):
  - Molecules can rotate, liquid will take the shape of the container
- Solid State (ice):
  - Molecules have fixed positions, solid has its own shape
- Change from one state to another:
  - Effect of temperature



What Are Gas Hydrates?

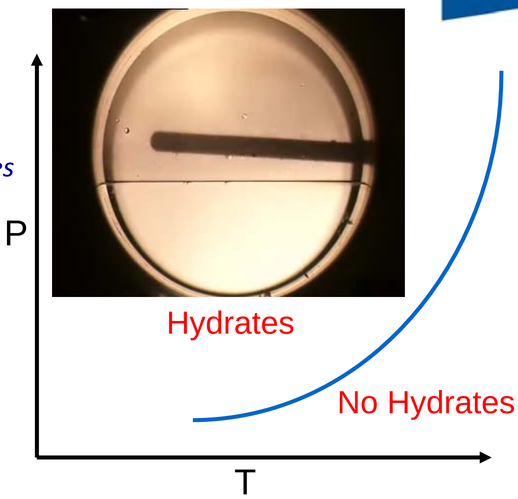
- Hydrates are crystalline solids wherein guest (generally gas) molecules are trapped in cages formed from hydrogen bonded water molecules (host)
- They look like ice, but unlike ice they can form at much higher temperatures
- Presence of gas molecules give extra attraction, hence stability, fixing the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





Necessary Conditions

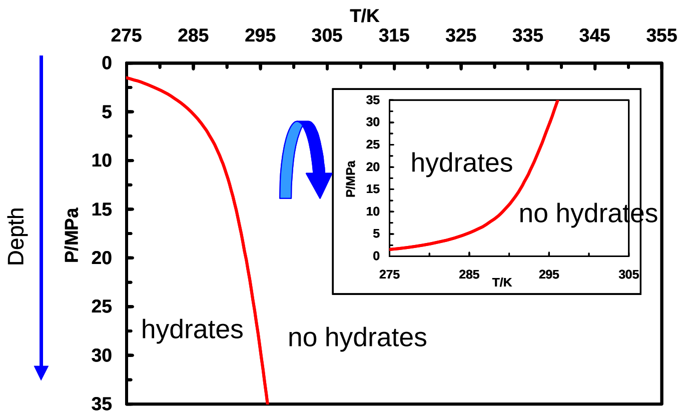
- The necessary conditions:
  - Presence of water or ice
  - *Suitably sized gas/liquid molecules* (such as C_1, C_2, C_3, C_4, CO_2, N_2, H_2S, etc.)
  - Suitable temperature and pressure conditions
- Temperature and pressure conditions is a function of gas/liquid and water compositions.



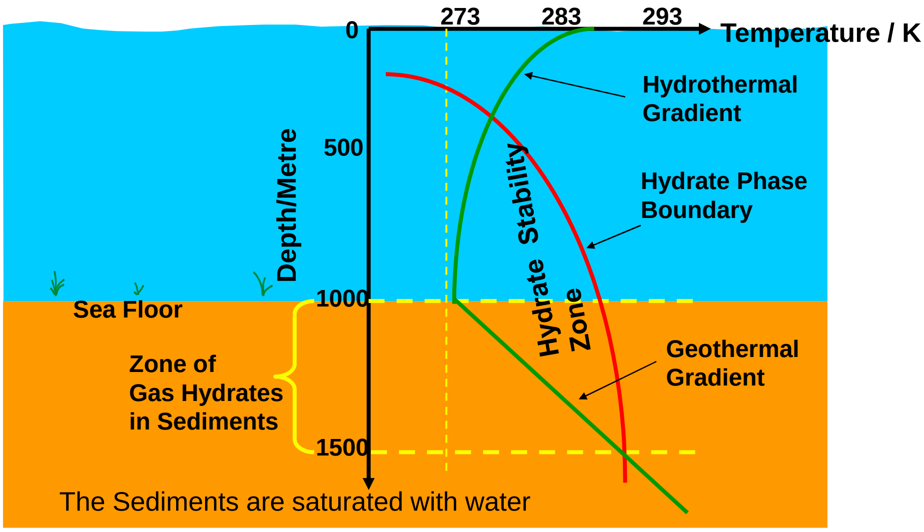
Hydrate phase boundary

Hydrates in Subsea Sediments

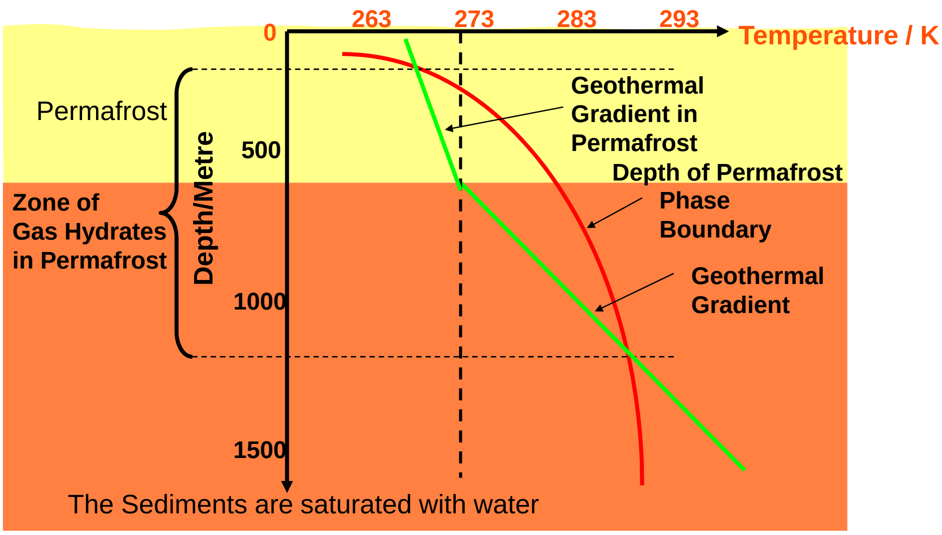
- There are massive quantities of gas hydrates in permafrost and ocean sediments.



Hydrate Stability Zone in Subsea Sediments

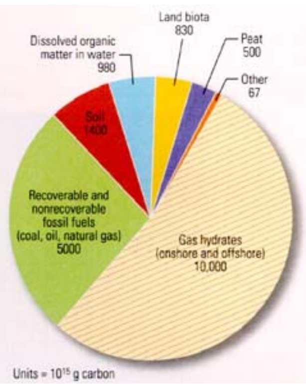


Hydrate Stability Zone in Permafrost

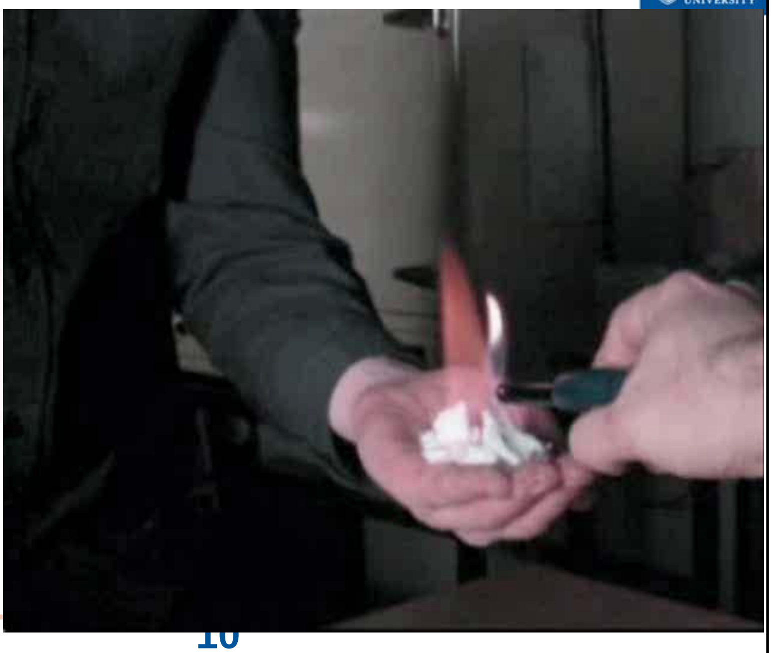


Methane Hydrate Discoveries

Methane Hydrates



Estimated at twice total fossil fuels



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

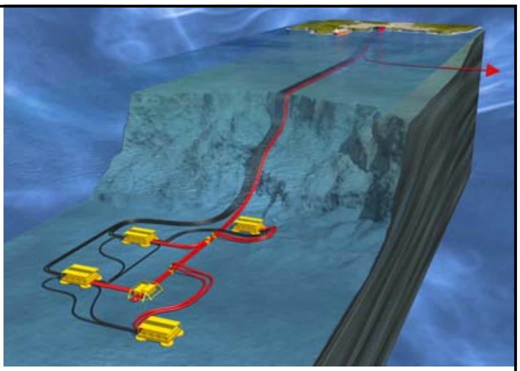
- Hydrate formation can block pipelines, wellbore/tubing
- Preventing production and/or normal operation
- Prevent access to wellbore

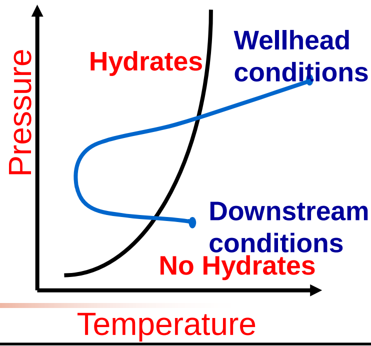
- Therefore, a hydrate blockage should avoided/removed
- There are various options associated with respect to avoiding/removing hydrate blockages

- 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: Requirements

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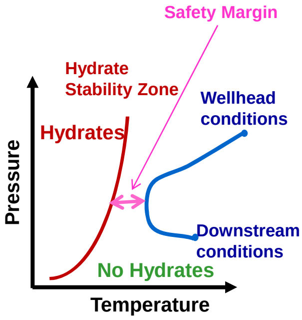
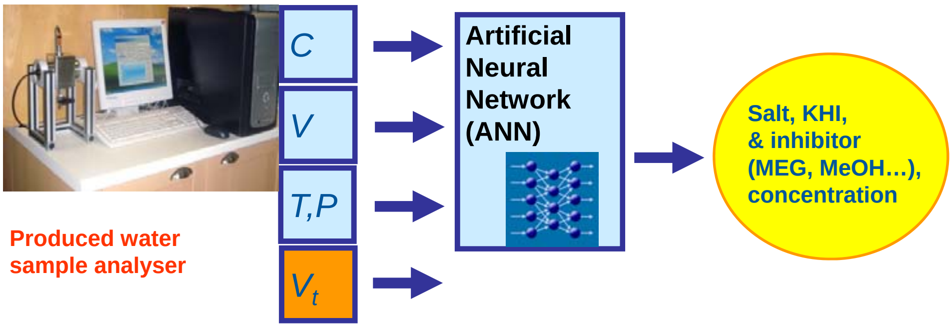
- Hydrate Stability Zone
  - *Composition of hydrocarbon phase*
  - *Hydrate inhibition characteristics of the aqueous*
    - *Salt*
    - *Chemical hydrate inhibitors*
  - *Pressure and temperature profile and/or the worst operation conditions*
    - *Computer simulation and/or P & T sensors*
- Why there could be a risk of hydrates
  - Uncertainty in water cut
  - Inhibitor partitioning in different phases
  - Equipment malfunctioning and/or human error
  - Changes to the system conditions
  - Off-spec Inhibitor



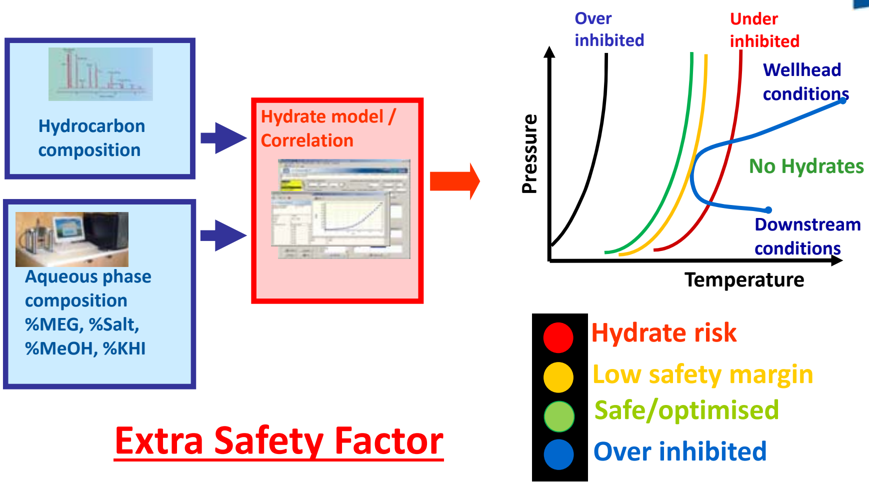
Extra Safety Factor if Measuring Actual Concentration of Inhibitor

Determining Inhibitor Concentration (HydraCHEK)



- 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 within few seconds

Hydrate Safety Margin Monitoring



- 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

Hydrate Inhibitor Monitoring System in a North Sea Gas Field

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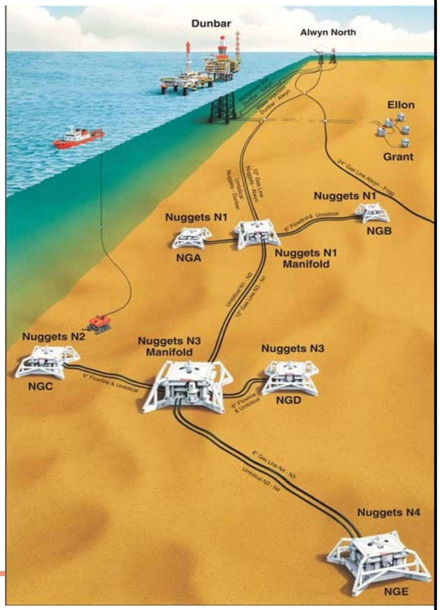
- **Location**
- 4 Gas bearing Eocene Structures
- 40 - 70 Km tie-back
- **Reservoir Characteristics**
- Frigg Sandstone
- Φ=30%, k=2000 - 4000mD; $K_v/K_h \approx 1$
- Reservoir Pressure =155 bara
- Temperature = 57 °C
- C_1 = 98%
- CGR = 2.1 E-6 Sm^3/Sm^3
- Strong aquifer influx



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Hydrate Phase Boundary

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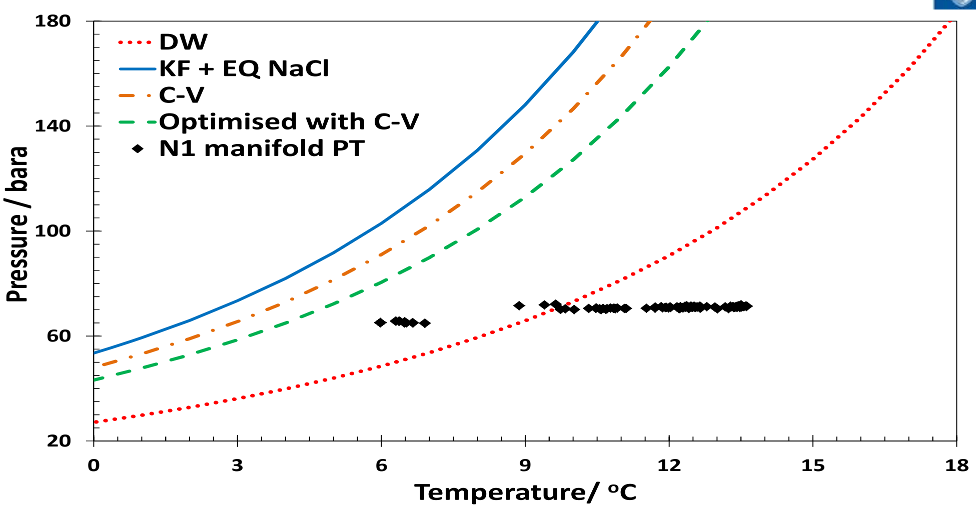

- Methanol injection was reduced to less than 5 wt% from designed 28 wt%
- Savings in the order of millions of GBP per year

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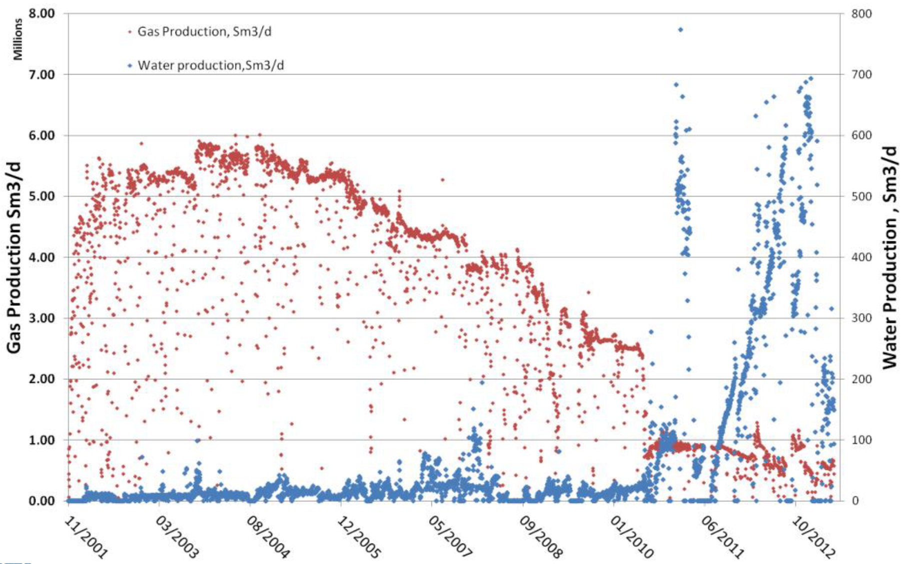
Minimising Methanol Injection

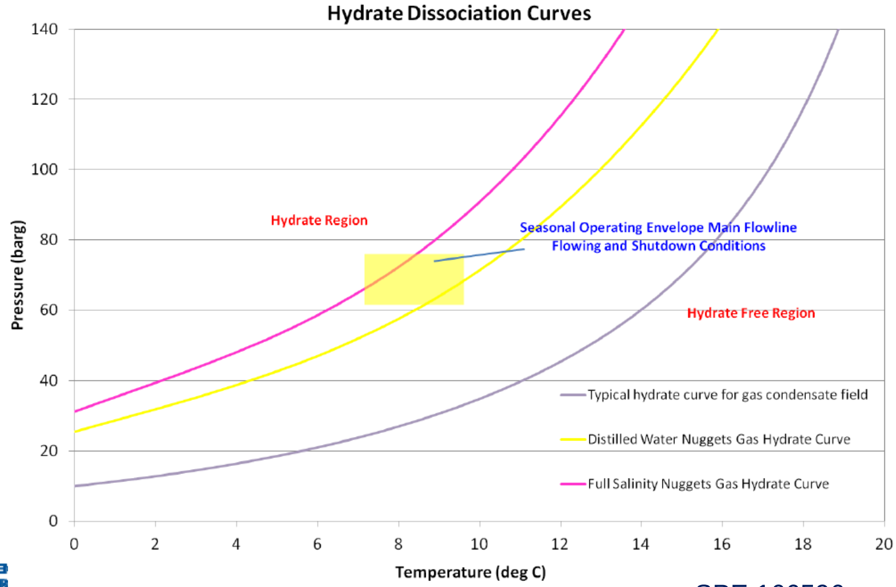
Nuggets Gas Field – Pushing the Operational Barriers
(SPE 166596)

- 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*

Field Production Profile



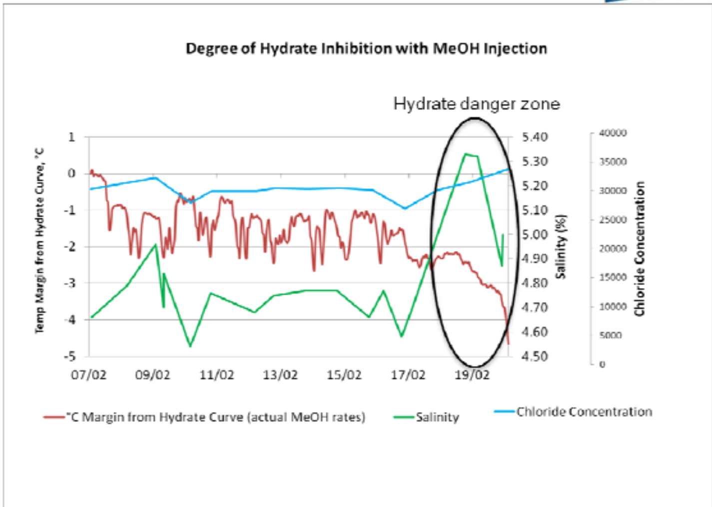
Operating Conditions



SPE 166596

Minimising Methanol Injection

Monitoring change in salinity was used for determining the concentration of hydrates in the slurry, while operating inside the hydrate stability zone



24-48 hours advanced warning prior to blockage

SPE 166596

Results

- The field life has been extended by three years with ***an incremental production of more than 3 million BOE in 2010-2013*** *(2% increase in Recovery Factor)*
- Steady production operations below nominal turndown and operating within hydrate zone
- Significant reduction of Methanol usage
- Field is still producing with the possibility of further prospects being tied-in to the existing facilities
- Extra income in excess of 140 millions GBP (based on rough calculations) from sale of the gas, payback period of less than 1 day
- Online HydraCHEK is ready for field trials

Online HydraCHEK

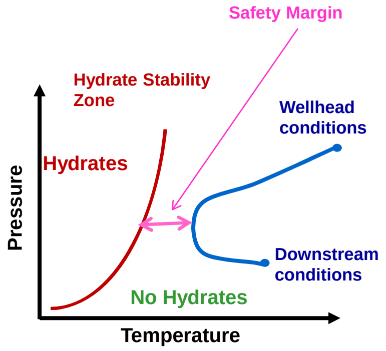
Trials of Safety Margin Monitoring Techniques

- 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.

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

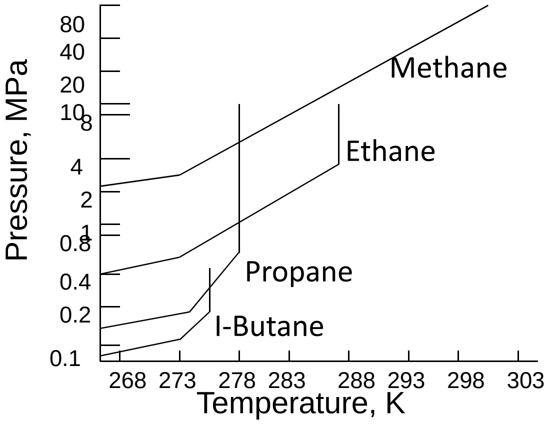


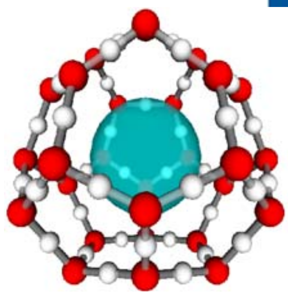
Hydrate Early Detection System

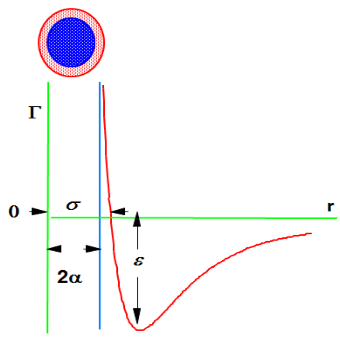
- It is believed initial hydrate formation does not result in pipeline blockage in many systems
- Therefore, detecting the signs of initial hydrate formation could provide an early warning system
- Hydrates prefer large and round molecules (e.g., C_3 and i-C_4 for sII hydrates) in their structures
- 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

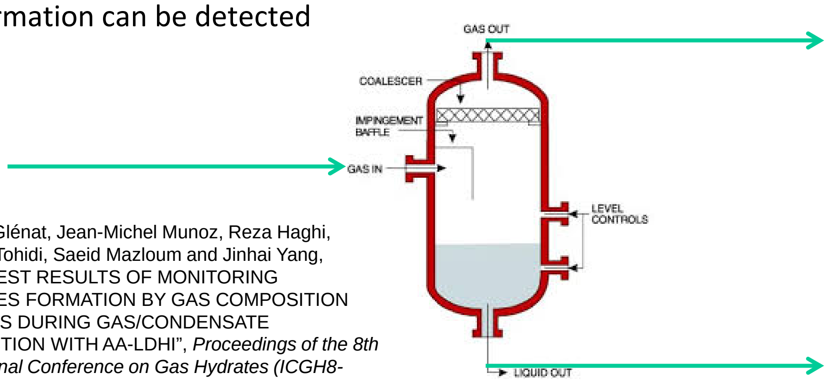






Hydrates in a Mature Field

- Very high gas to condensate ratios
- High water cut, hence switched to AA for Hydrate Blockage Prevention
- Online Gas Chromatograph was installed on gas outlet to see if hydrate formation can be detected



Philippe Glénat, Jean-Michel Munoz, Reza Haghi, Bahman Tohidi, Saeid Mazloum and Jinhai Yang, "FIELD TEST RESULTS OF MONITORING HYDRATES FORMATION BY GAS COMPOSITION CHANGES DURING GAS/CONDENSATE PRODUCTION WITH AA-LDHI", *Proceedings of the 8th International Conference on Gas Hydrates (ICGH8-2014), Beijing, China, 28 July - 1 August, 2014*

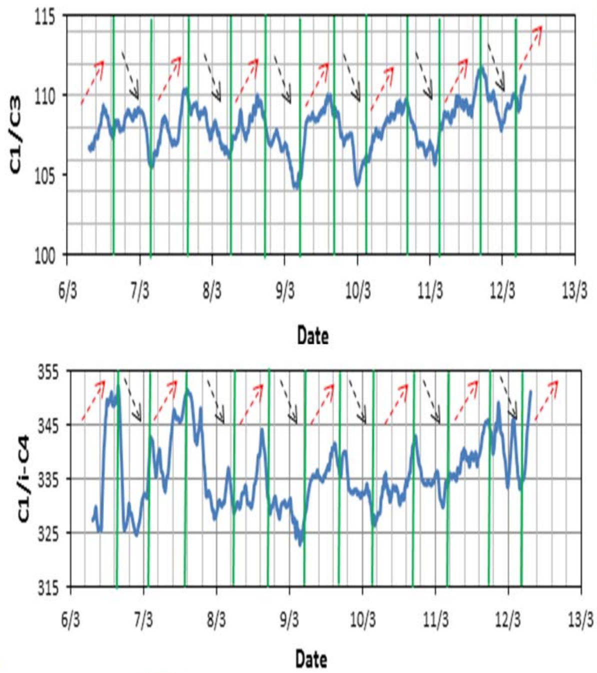
Results

sII hydrates use C_3 and iC_4, hence an increase in C_1/C_3 and C_1/iC_4 ratios

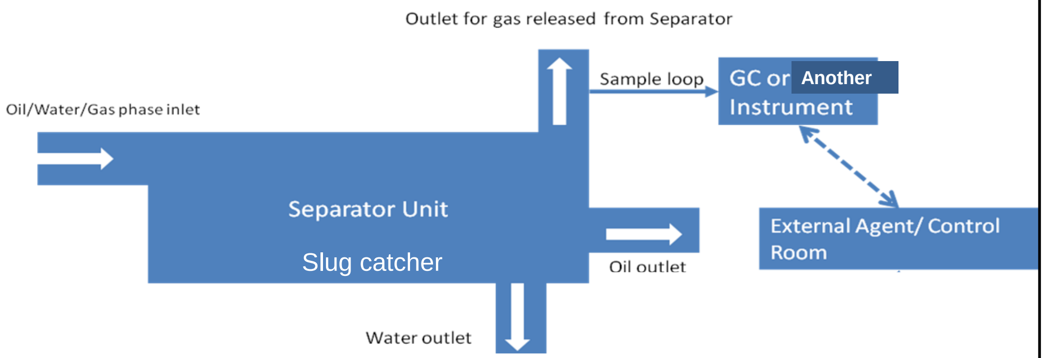
Initially, the results look scattered

In , these are changes during day and night times

Hydrates are forming during time times when the temperature is low



Potential Implementation Configuration

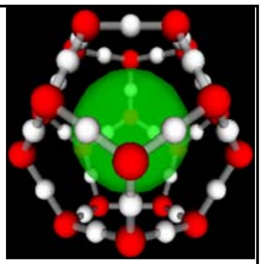


Hydrate formation results in a reduction in the concentration of large and round molecules in the gas phase

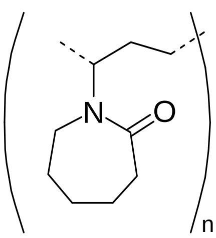
Summary/Conclusions

- 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

Kinetic Hydrate Inhibitors (KHI)



- Affect hydrate nucleation & growth
- Two conventional formulations are
  - *Poly(N-Vinylcaprolactam) = PVCap*
  - *Poly(N-Vinylpyrrolidone) = PVP*



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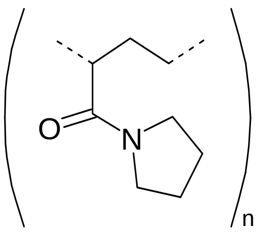

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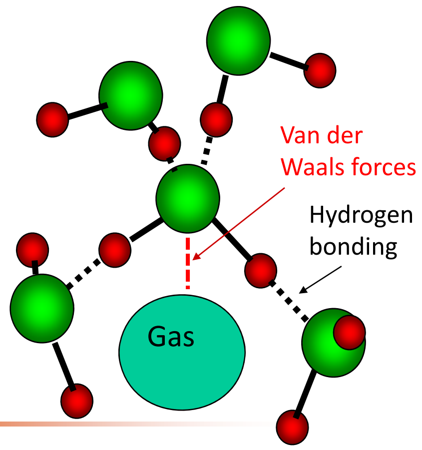
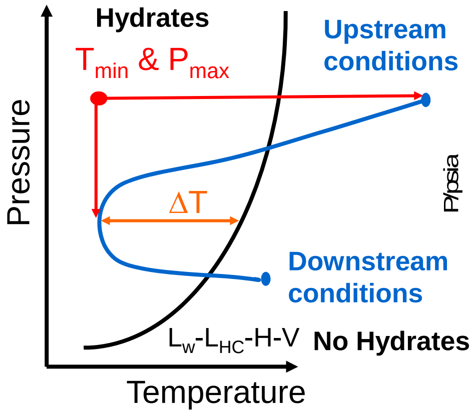
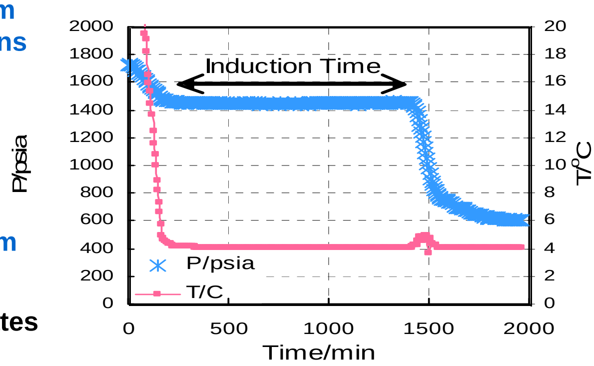


Avoiding Hydrate Problems-Kinetic Hydrate Inhibitors

Kinetic Hydrate Inhibitors affect nucleation and/or growth stage(s)

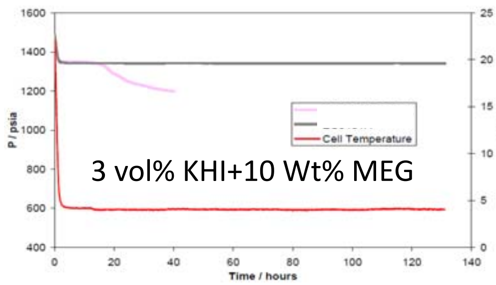


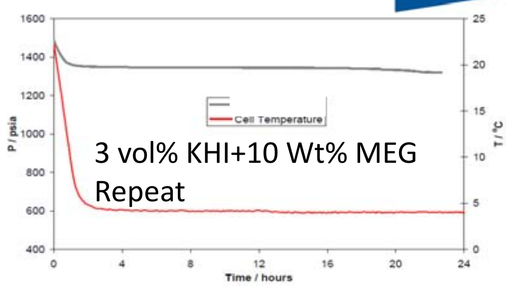


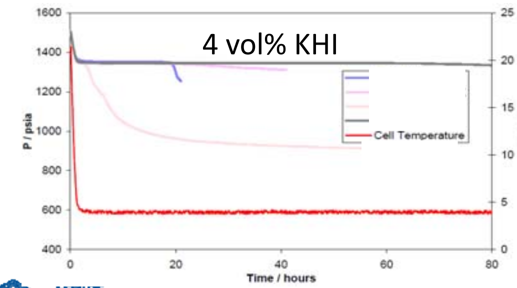
Test Conditions: Minimum Temperature & Maximum Pressure!!!

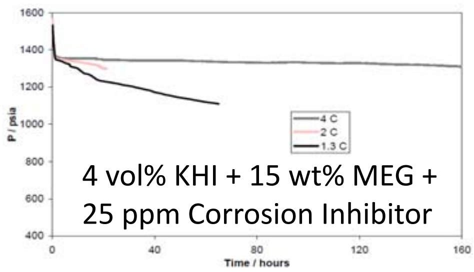
Induction time should be longer than the fluid residence time!

KHI Performance Testing







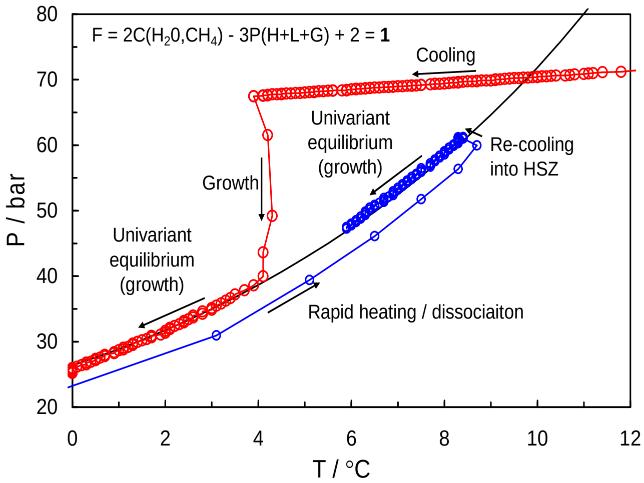


KHIs: New CGI Approach Test Procedures

Nucleation vs Growth

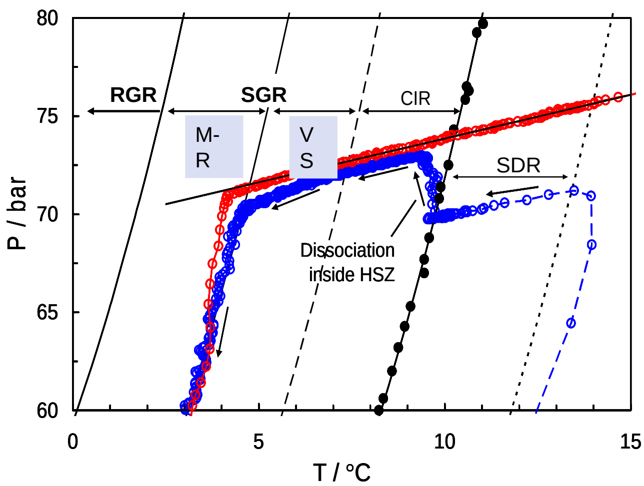
Nucleation: stochastic in the absence of nucleation site
Hydrate nuclei are small and cannot cause blockage

Growth is potentially ordered under low driving force
Growth can result in large hydrate blockages



Growth/dissociation behaviour in a simple methane-water system

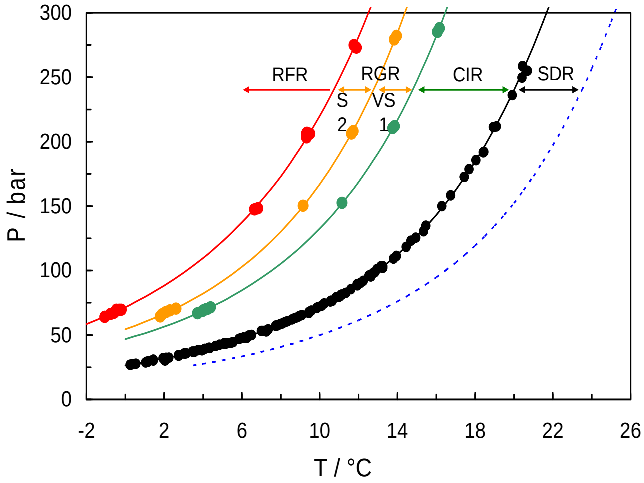
KHIs: New CGI Approach Test Procedures



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

Determination of CGI regions for 0.25 mass% PVCap with methane

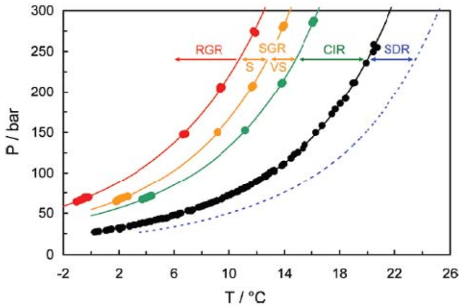
New CGI Approach: Methane-PVCap Systems

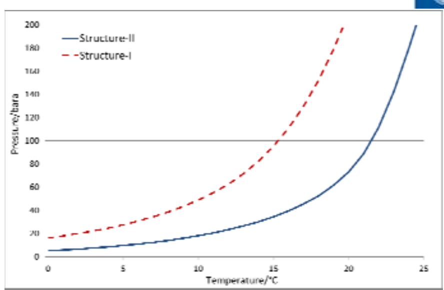


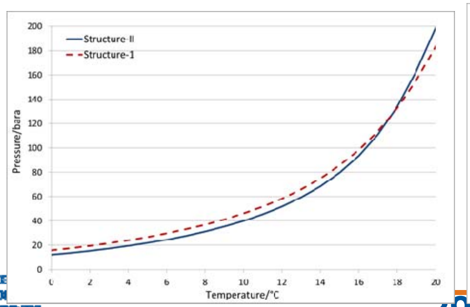
Experimental CGI regions for 1.0 mass% PVCap with methane

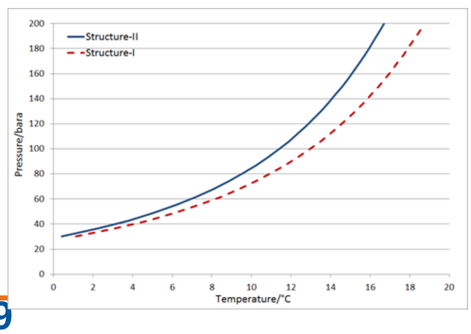
CGI boundaries at ΔT_{sub} = ~5.3 C and ~7.2 C are shared with 0.5% PVCap. Related to underlying crystal growth patterns?

KHIs: Effect of Hydrate Structure

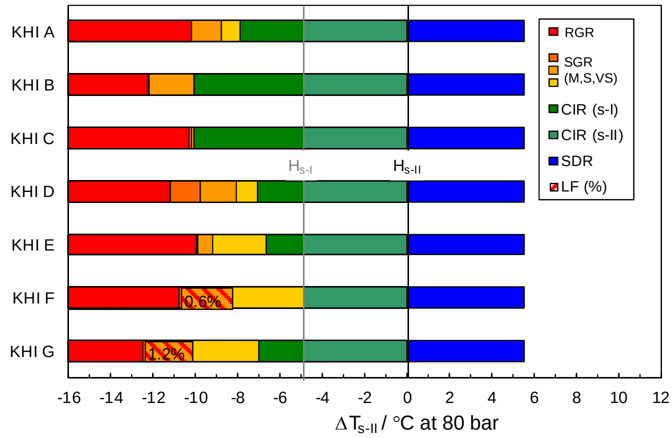








KHIs: Effect of KHI Formulation



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)

CENTRE FOR GAS HYDRATE RESEARCH

KHIs: Opportunities and Challenges

KHI in Shut-ins and Re-Starts

Past

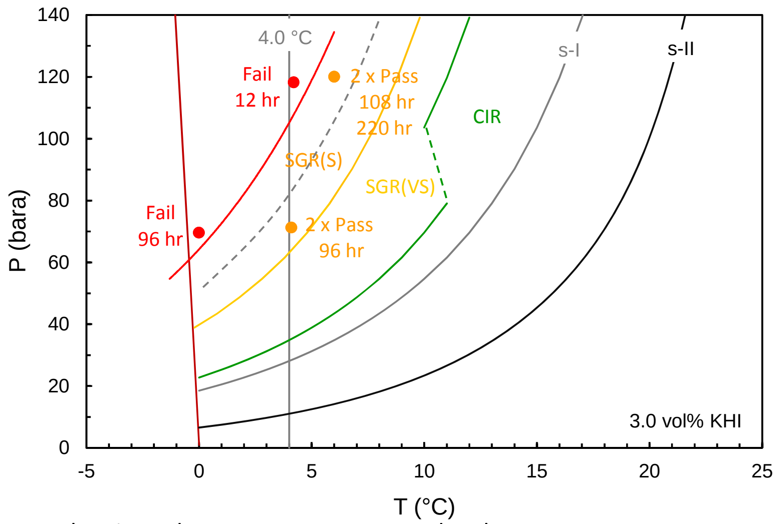
- One of the previously reported weaknesses was that KHIs cannot prevent hydrate formation in long shut-ins
- Hence, pipeline pressure should be reduced to below hydrate stability pressure at seabed temperature
- A lot of gas flaring
- Slow re-start to warm up the pipeline (potentially more gas flaring)

Now

- We now know that KHIs can act as thermodynamic inhibitor within CIR (Continuous Inhibition Region)
- Hence, increasing the shut-in pressure, reducing the flaring
- Faster re-start, as we have some measure on rate of hydrate formation

CENTRE FOR GAS HYDRATE RESEARCH

KHIs in Shut-ins and Re-Starts



Past: shut-in and restart pressure around 10 bar
Now: shut-in pressure around 32 bar, re-start pressure 60 to 80 bar

KHIs: Opportunities and Challenges

KHI in Produced Water Processing/Re-Injection

Past

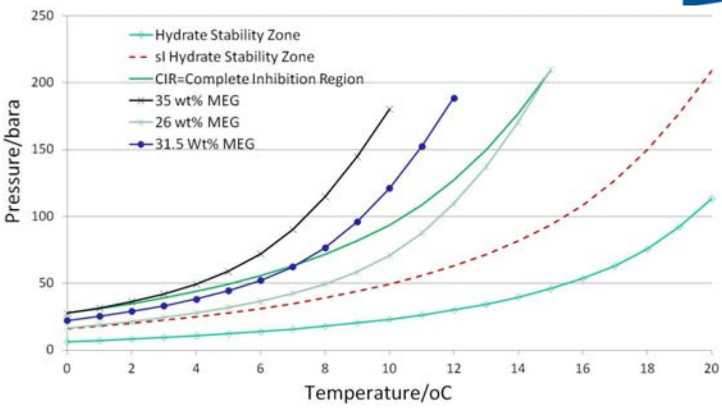
- KHIs are polymers and their cloud point could be around 40 °C
- They can cause problem in pumps inlet strainers in hot environment
- They can cause blockage in produced water re-injection wells

Now

- We can now remove KHIs from produced water by a solvent extraction technique
- The technique is based on adding a solvent (e.g., organic high carbon-chain alcohols) 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 (with an average equivalent of 31.5 wt%), depending on the operating (or worst) conditions. The actual performance of KHI is likely to be higher as KHI and MEG and are good synergic, but this will require further testing.

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 (e.g., organic high carbon-chain alcohols) to the aqueous phase after 3-phase separator
- The produced water, free of KHI, can be sent to MEG regeneration units
- The removed KHI can be recovered and reused

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 Produced Water Re-Injection (PWRI) problems and allows combined KHI+MEG allocations
- KHI removal potential could play a major role in future KHI design

Some References & Acknowledgements

Tohidi B., Anderson R., Mozaffar H., Tohidi F., "THE RETURN OF KINETIC HYDRATE INHIBITORS", *Proceedings of the 8th International Conference on Gas Hydrates (ICGH8-2014), Beijing, China, 28 July - 1 August, 2014.*

Yang J., Mazloum S., Chapoy A., Tohidi B., "MINIMIZING HYDRATE INHIBITOR INJECTION RATES", IPTC 17835-MS, the International Petroleum Technology Conference held in Kuala Lumpur, Malaysia, 10-12 December 2014.

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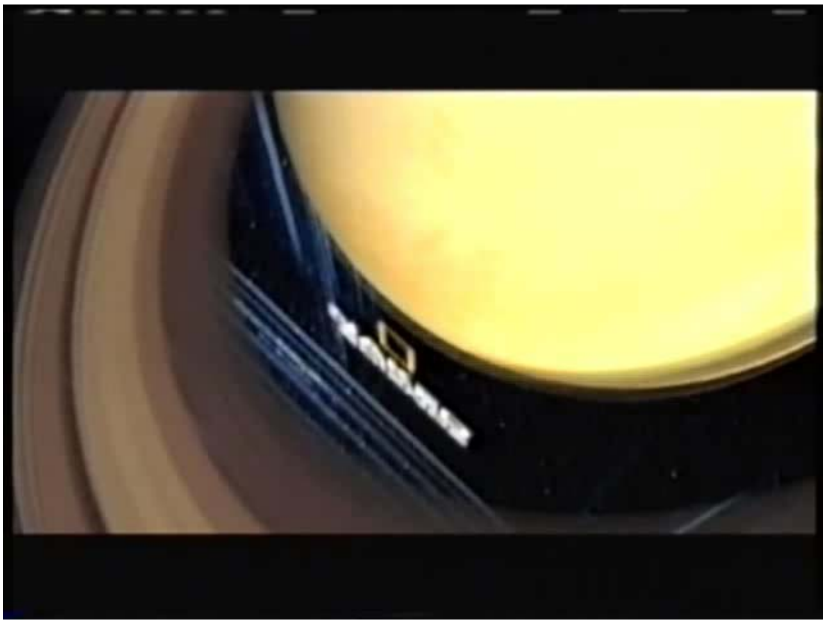

https://www.youtube.com/watch?v=YB1GLbHCdVI