



The University of Texas at Austin  
Center for Subsurface Energy  
and the Environment  
*Cockrell School of Engineering*

# **SIGNIFICANCE OF HYDRATE FORMATION DURING CO<sub>2</sub> STORAGE IN DEPLETED GAS STORAGE**

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**JANUARY 23, 2024**

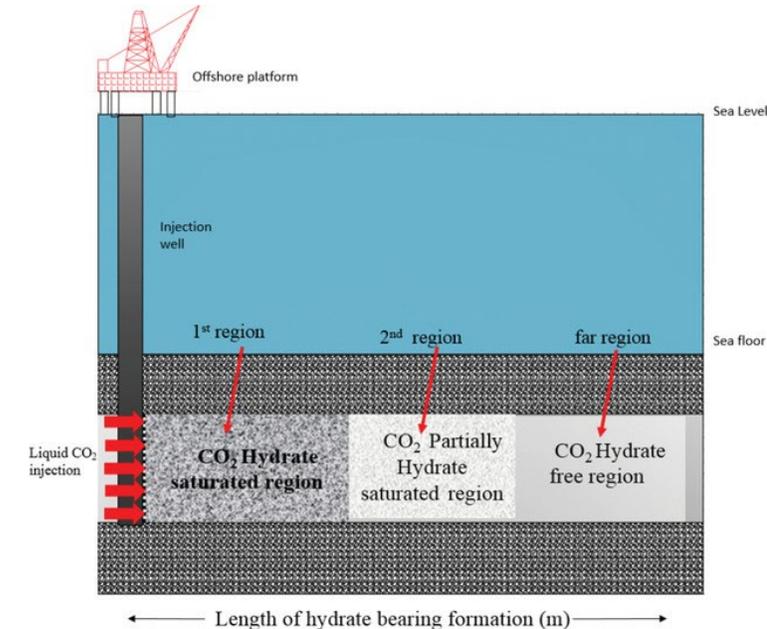
# Problem Statement

- Gas hydrates are a crystalline solid formed of water and gas.
- Injection of high-pressure cold CO<sub>2</sub> into porous formations can lead to the formation of hydrates.
- This effect intensifies the Joule-Thomson cooling which causes a drop in temperature, and can potentially lead to hydrate conditions.
- Hydrates can lead to severe injectivity reduction and even plugging of the reservoir areas surrounding the well.

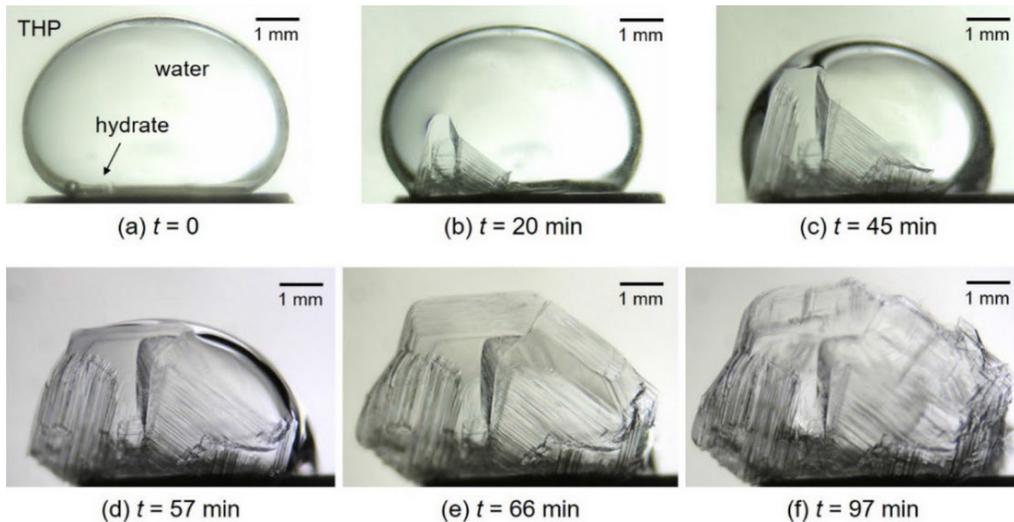
## Hydrates in the pipelines/wellbore



## Hydrates in the porous media



Ahmad et al. (2019)



Maruyama et al. (2021)

# Hydrate modeling and risk assessment approaches

Phase diagram approach (qualitative):

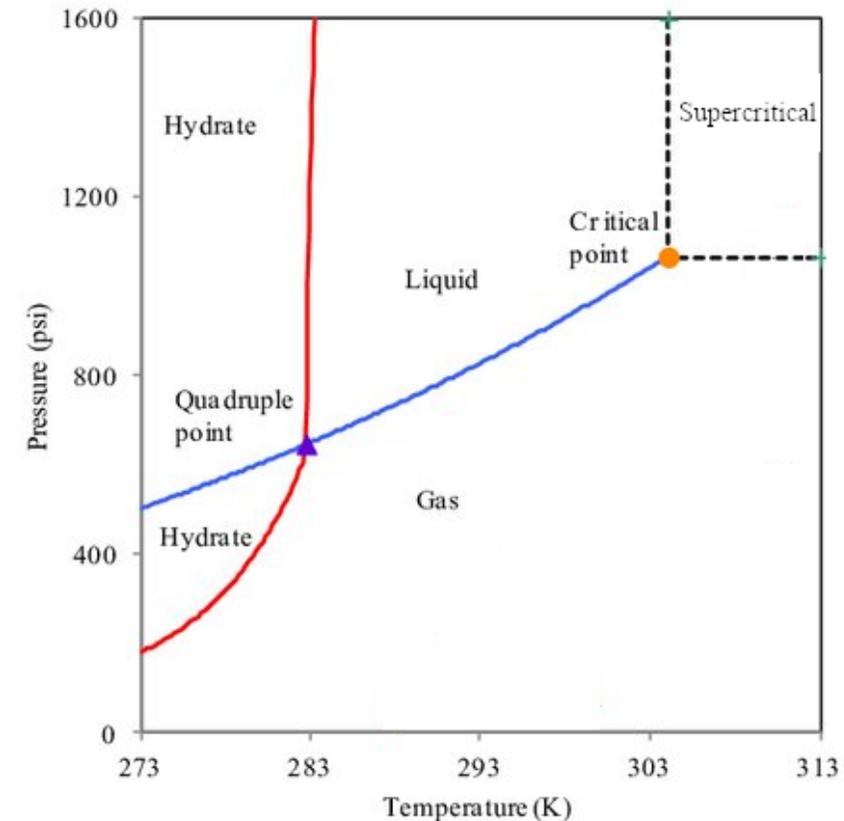
- Check reservoir conditions to determine risk of hydrates.
- Can use activity-based model to estimate phase diagram of gas mixtures and effect of inhibitors.

Flash calculation:

- Combines conventional EoS flash approach with the van der Waals and Platteeuw (1959) model.

Hydrate kinetics:

- Use kinetic models to quantify the amount of hydrate formed or dissociated over time.
- Both equilibrium and transient models are reported in the literature.



modified from Ramachandran et al. (2014)

# CMG reservoir simulator capabilities



- GEM features

- Fully compositional thermal model
  - Hydrocarbon phases modeled with PR or SRK EoS
  - No mass transfer between the water phase and the HC phases
  - Water vaporization can be included with the OGW flash



- STARS features

- Thermal model with Joule-Thomson (Lee-Kesler model)
  - SRK EoS without binary interaction coefficients for gas phase
  - Liquid phases are modeled as slightly compressible fluids
  - K-values used for phase equilibrium (includes water-gas equilibrium for dry-out)
  - Kinetic model based on Kim et al. (1987)

# VERIFICATION OF THE THERMAL MODEL WITH TOUGH2

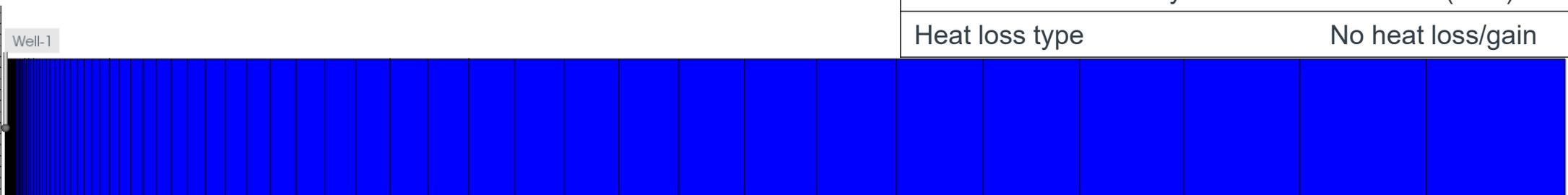
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# Comparison with TOUGH2 (Open Boundary)

- Constant injection rate (3 kg/s)
- CH<sub>4</sub> gas reservoir and CO<sub>2</sub> is injected
- Initial water saturation is 0.2
- Constant diffusion coefficients
- Include heat conduction
- Data taken from:
  - “Oldenburg, C. M., Joule-Thomson cooling due to CO<sub>2</sub> injection into natural gas reservoirs. Energy Conversion & Management, Vol 48, pp. 1808-1815, 2007”

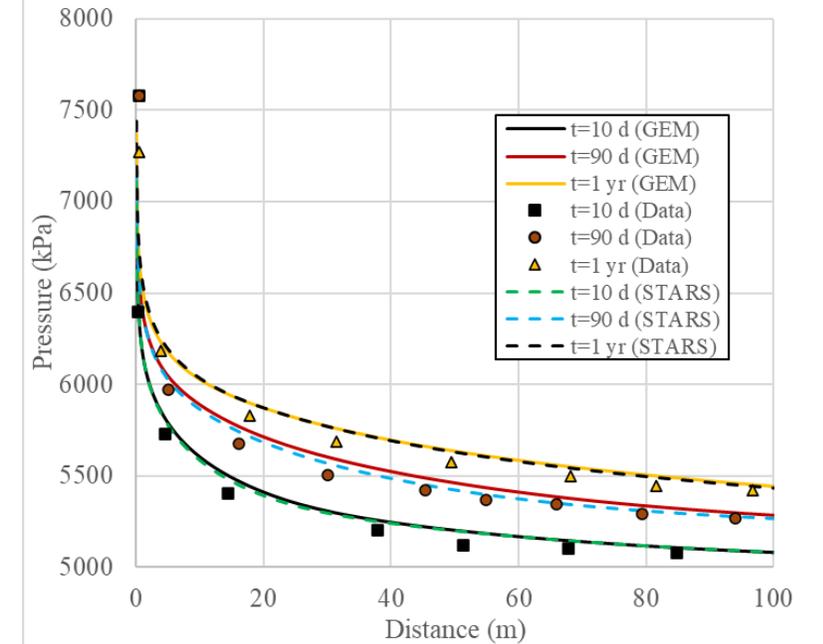
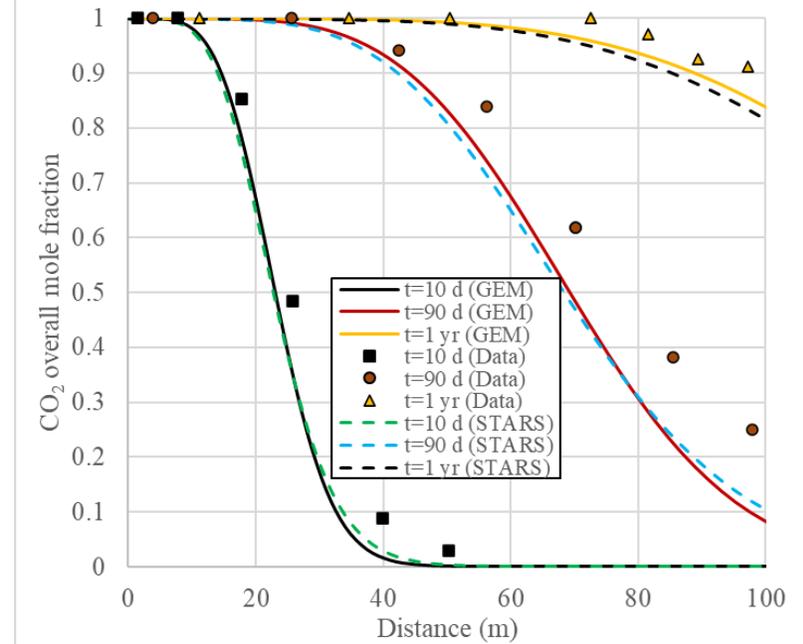
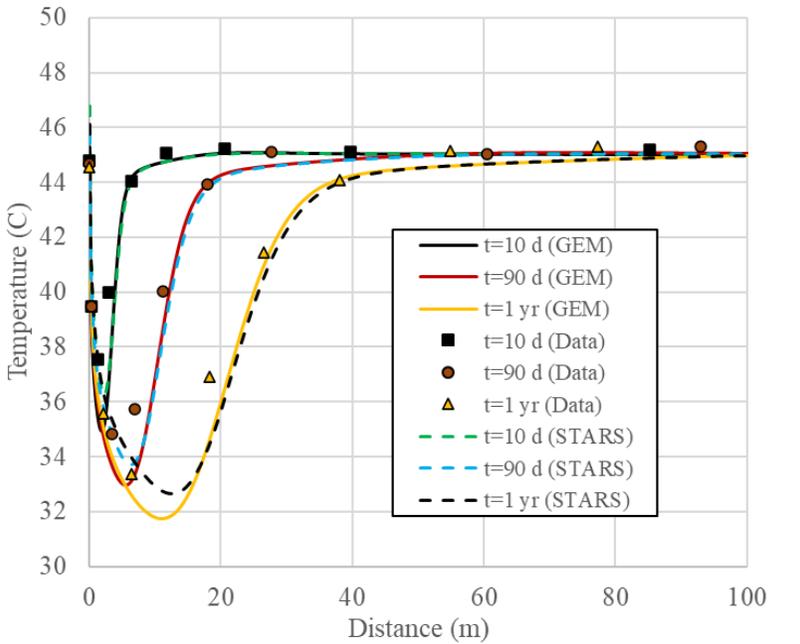
| Properties             | Value  |
|------------------------|--|
| Reservoir temperature  | 45 C   |
| Injection temperature  | 45 C   |
| Well radius            | 0.0097 m   |
| Reservoir radius       | 1130 m   |
| Thickness              | 50 m   |
| Porosity               | 0.3  |
| Permeability           | 5 mD   |
| Initial pressure       | 5 Mpa  |
| Injection rate         | 13.9527x10 <sup>4</sup> sm <sup>3</sup> /d (3 kg CO <sub>2</sub> /s)   |
| Production rate        | 7.1468x10 <sup>4</sup> sm <sup>3</sup> /d (0.56 kg CH <sub>4</sub> /s) |
| Rock heat capacity     | 1000 J/(kg°C)  |
| Rock heat conductivity | 2.51 W/(m°C)   |
| Heat loss type         | No heat loss/gain  |



# STARS and GEM vs TOUGH2 (Open Boundary)

## Temperature, CO<sub>2</sub> Mole fraction, and Pressure profiles

\*Data refers to TOUGH2



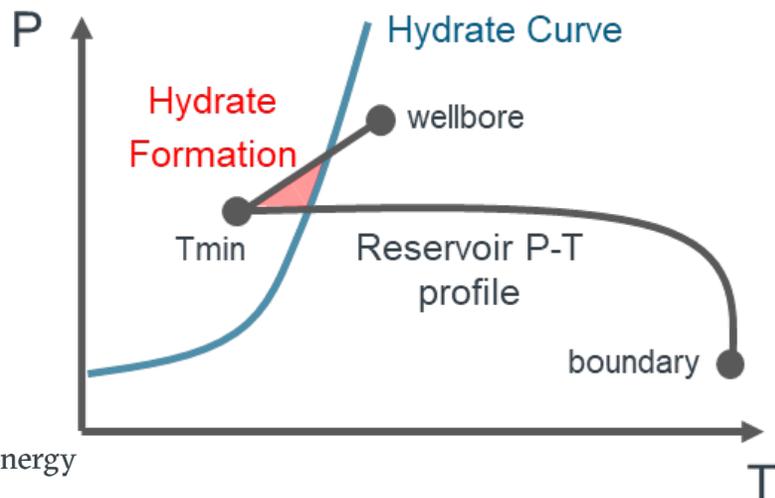
- GEM and STARS show good agreement of results.
- Discrepancies with TOUGH2 could be caused by different grid size and differences in property calculation between the simulators.

# HYDRATE RISK ASSESSMENT WITH GEM

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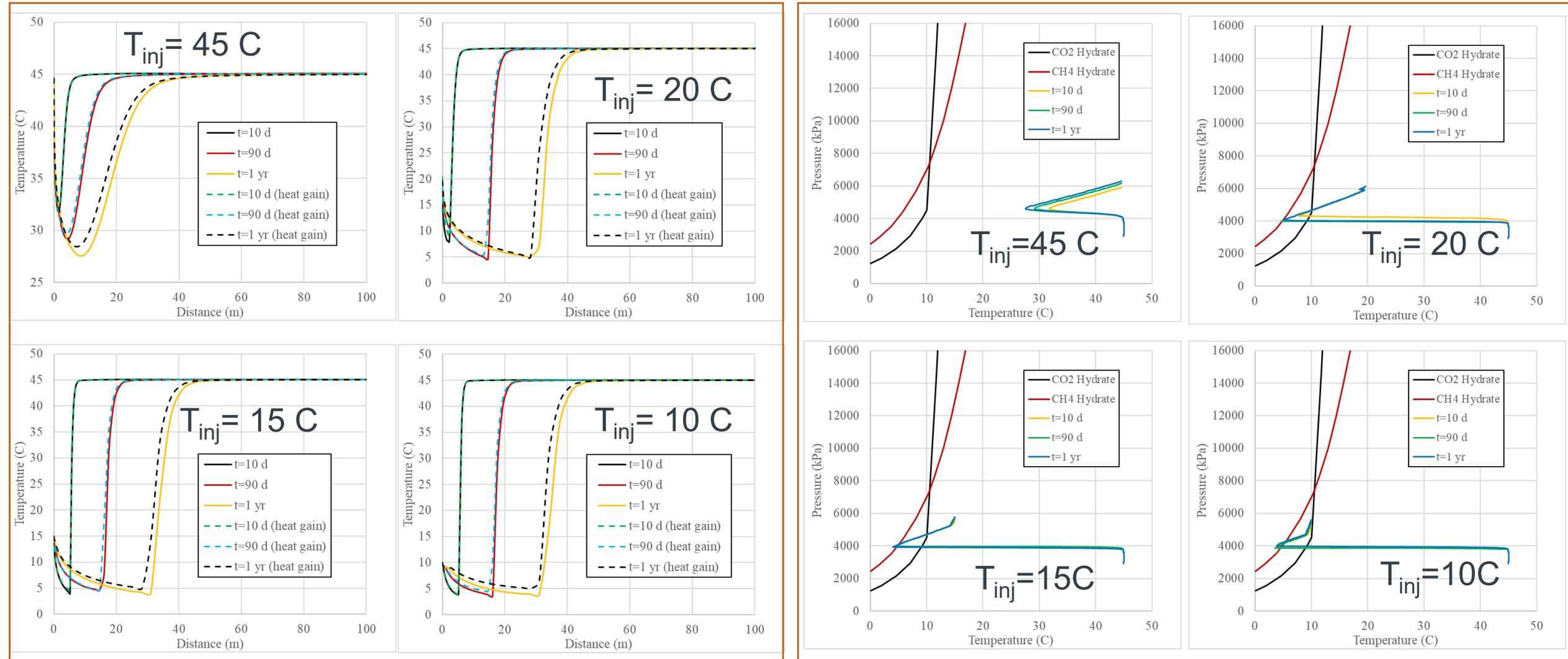
# Hydrate Risk Assessment with CMG GEM (Phase diagram approach)

- Constant rate CO<sub>2</sub> injection
- Initial fluid saturations = S<sub>w</sub> : 0.2 and CH<sub>4</sub>
- PR EoS is used
- Model heat conduction
- **Liquid CO<sub>2</sub> was observed near the wellbore which reduces JT cooling**
- **Lower initial reservoir pressure intensifies JT cooling**



| Properties                              | Value                       |
|---|-----------------------------|
| Reservoir temperature                   | 45 C                        |
| Injection temperature                   | <b>10, 15, 20, and 45 C</b> |
| Well radius                             | 0.0097 m                    |
| Reservoir radius                        | 1130 m                      |
| Thickness                               | 50 m                        |
| Porosity                                | 0.3                         |
| Permeability                            | 5 mD                        |
| Initial pressure                        | <b>3 and 5 Mpa</b>          |
| Injection rate                          | 3 kg CO <sub>2</sub> /s     |
| Production rate                         | 0.56 kg CH <sub>4</sub> /s  |
| Rock heat capacity                      | 1000 J/(kg°C)               |
| Rock heat conductivity                  | 2.51 W/(m°C)                |
| Heat exchange                           | Sensitivity                 |
| Under/overburden rock heat capacity     | 1000 J/(kg°C)               |
| Under/overburden rock heat conductivity | 2.51 W/(m°C)                |

# Temperature Profile and PT diagram: $T_{res} = 45^{\circ}\text{C}$ ; $P_{res} = 3\text{MPa}$



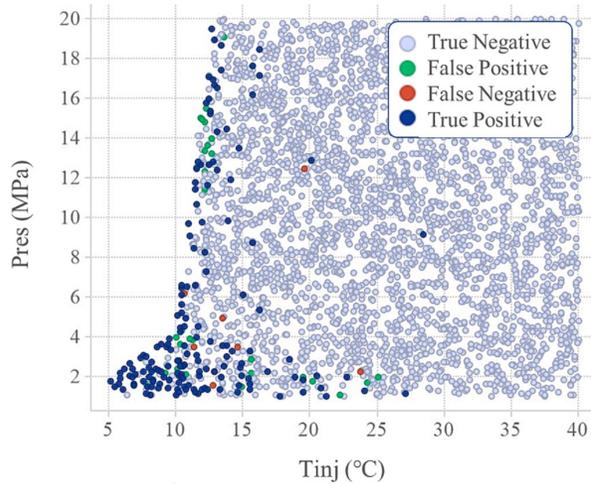
Min temperature is about  $3^{\circ}\text{C}$  even as  $T_{inj}$  is reduced

JT cooling leads to hydrate formation

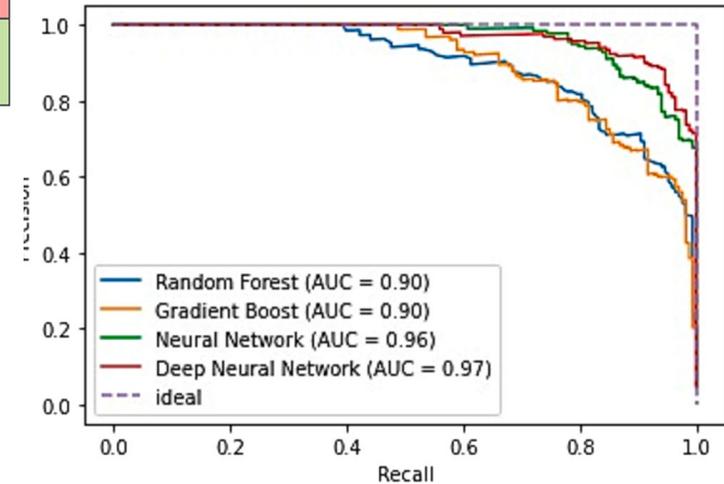
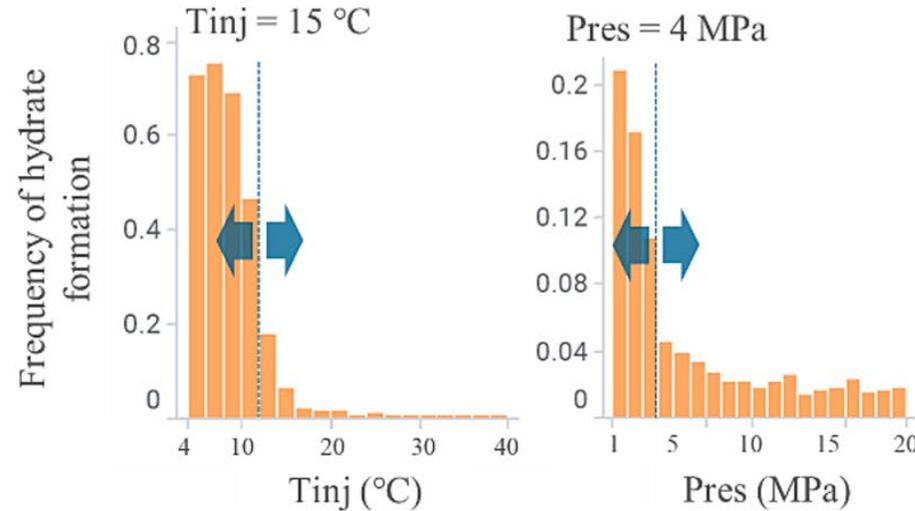
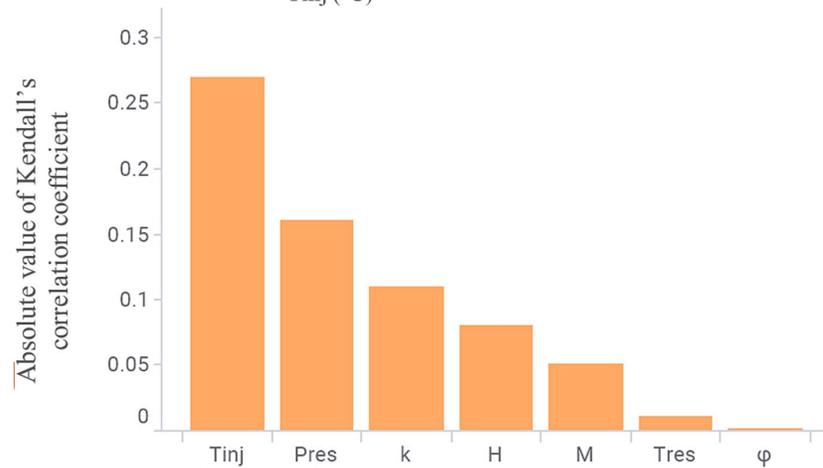
# Run Simulations to train a Machine Learning tool

“Yamada et al., Development of a hydrate risk assessment tool based on machine learning for CO<sub>2</sub> storage in depleted gas reservoirs. Fuel, Vol 357, 2024”

- A sensitivity analysis with **18,532 scenarios** was performed with CMG-GEM.
- ML models tested: random forest, gradient boosting, neural network, deep neural network.



|        |                                      | Predicted                          |                                      |
|--------|--------------------------------------|------------------------------------|--------------------------------------|
|        |                                      | Negative<br>(limited hydrate risk) | Positive<br>(potential hydrate risk) |
| Actual | Negative<br>(limited hydrate risk)   | 3325                               | 30                                   |
|        | Positive<br>(potential hydrate risk) | 8                                  | 160                                  |



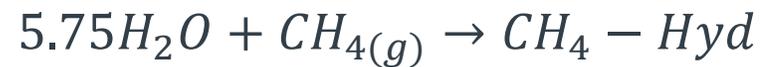
# HYDRATE MODELING WITH STARS

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# Hydrate kinetic model

- Use Kozeny-Carman equation to calculate permeability changes as a function of porosity.
- Reactions to model hydrate formation and dissociation.

Methane hydrate formation:



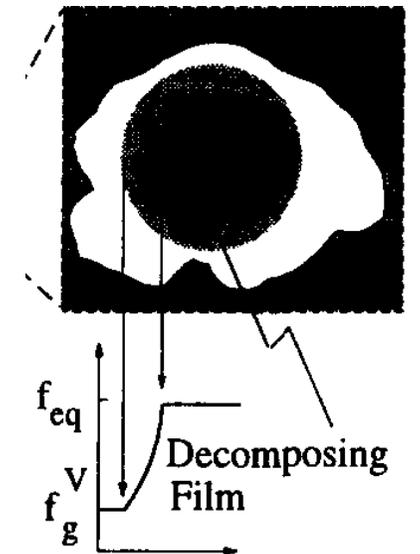
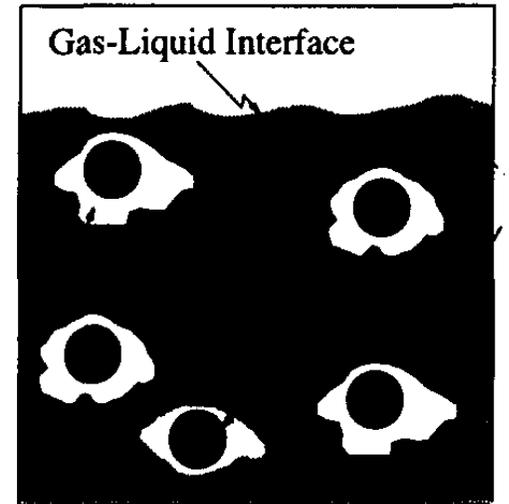
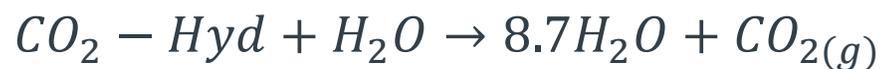
Methane hydrate dissolution:



CO<sub>2</sub> hydrate formation:



CO<sub>2</sub> hydrate dissolution:

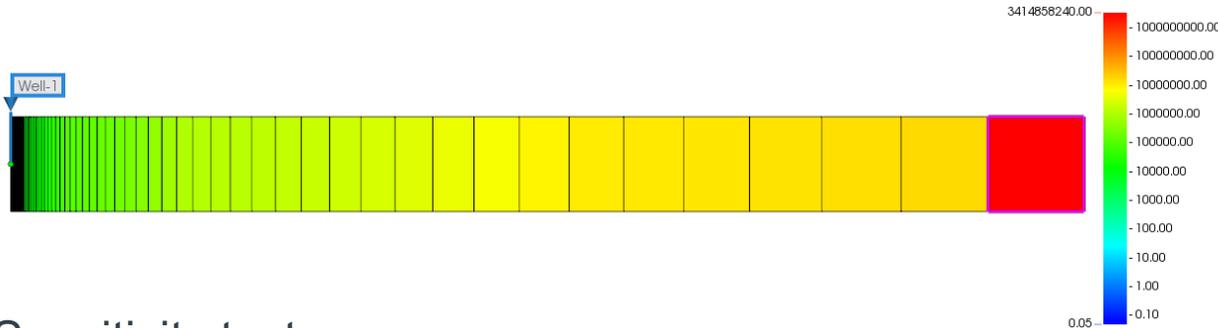


Bishnoi and Natarajan (1996)

# Demonstration case

“Indina et al., On The Significance of Hydrate Formation/Dissociation during CO<sub>2</sub> Injection in Depleted Gas Reservoirs. 2024 Oman Petroleum & Energy Show (OPES), SPE-218550-MS.”

- 100x1x1 grid with grid refinement
- Porosity changes may result in permeability change
- Model heat conduction
- Infinite reservoir is modeled



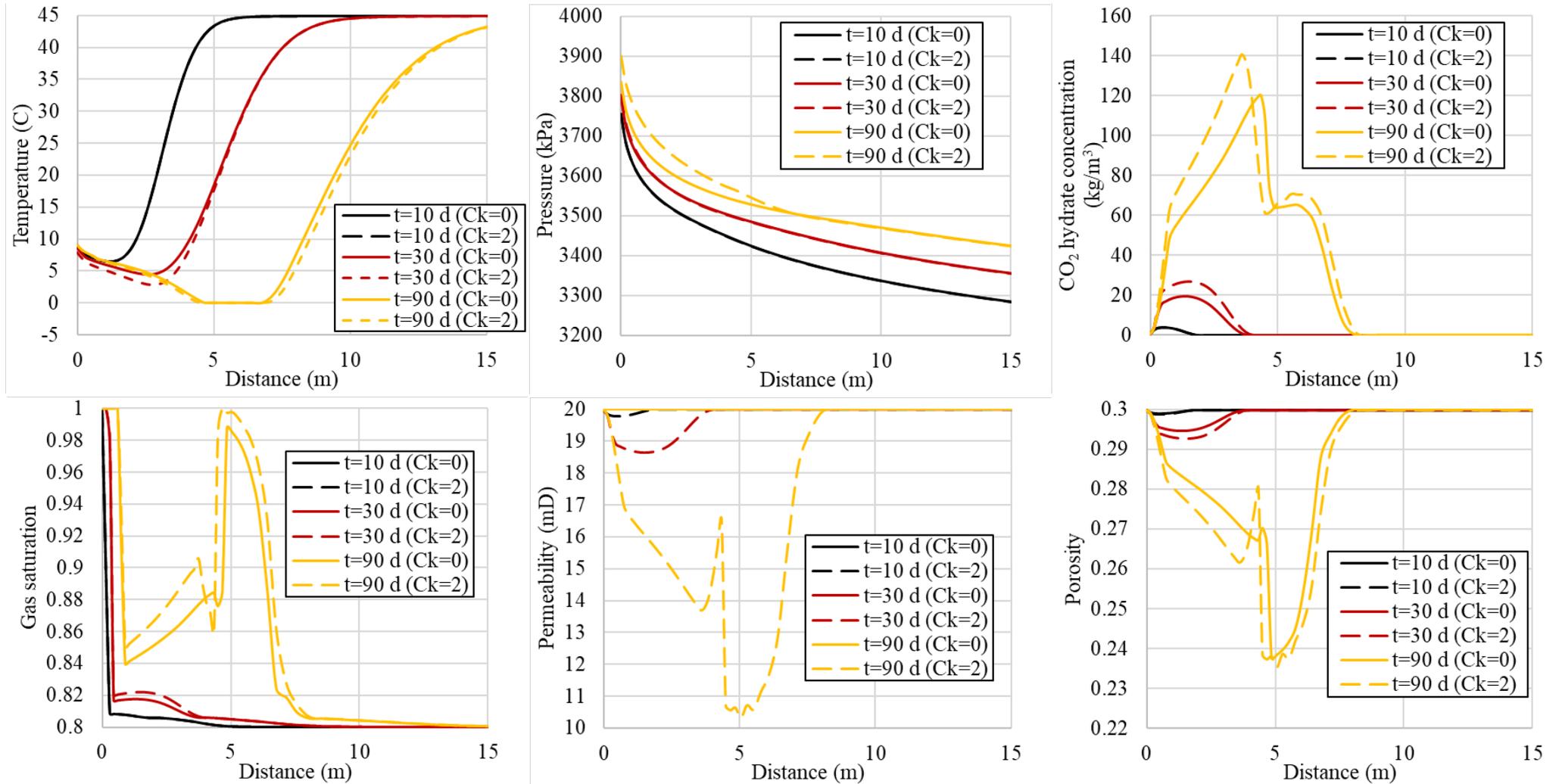
## Sensitivity tests:

- Heat exchange with over and underburden formations
- Permeability reduction
- Grid geometry

|                                 | Value                   |
|---------------------------------|-------------------------|
| Reservoir temperature           | 45 C                    |
| Initial water saturation        | 0.2                     |
| Initial hydrocarbon composition | 100% CH <sub>4</sub>    |
| Injection temperature           | 10 C                    |
| Well radius                     | 0.0097 m                |
| Porosity                        | 0.3                     |
| Permeability                    | 20 mD                   |
| Initial pressure                | 3 Mpa                   |
| Injection rate                  | 3 kg CO <sub>2</sub> /s |
| Rock heat capacity              | 1000 J/(kg°C)           |
| Rock heat conductivity          | 2.51                    |
| Base/Cap rock heat capacity     | 1000 J/(kg°C)           |
| Base/Cap rock heat conductivity | 2.51 W/(m°C)            |

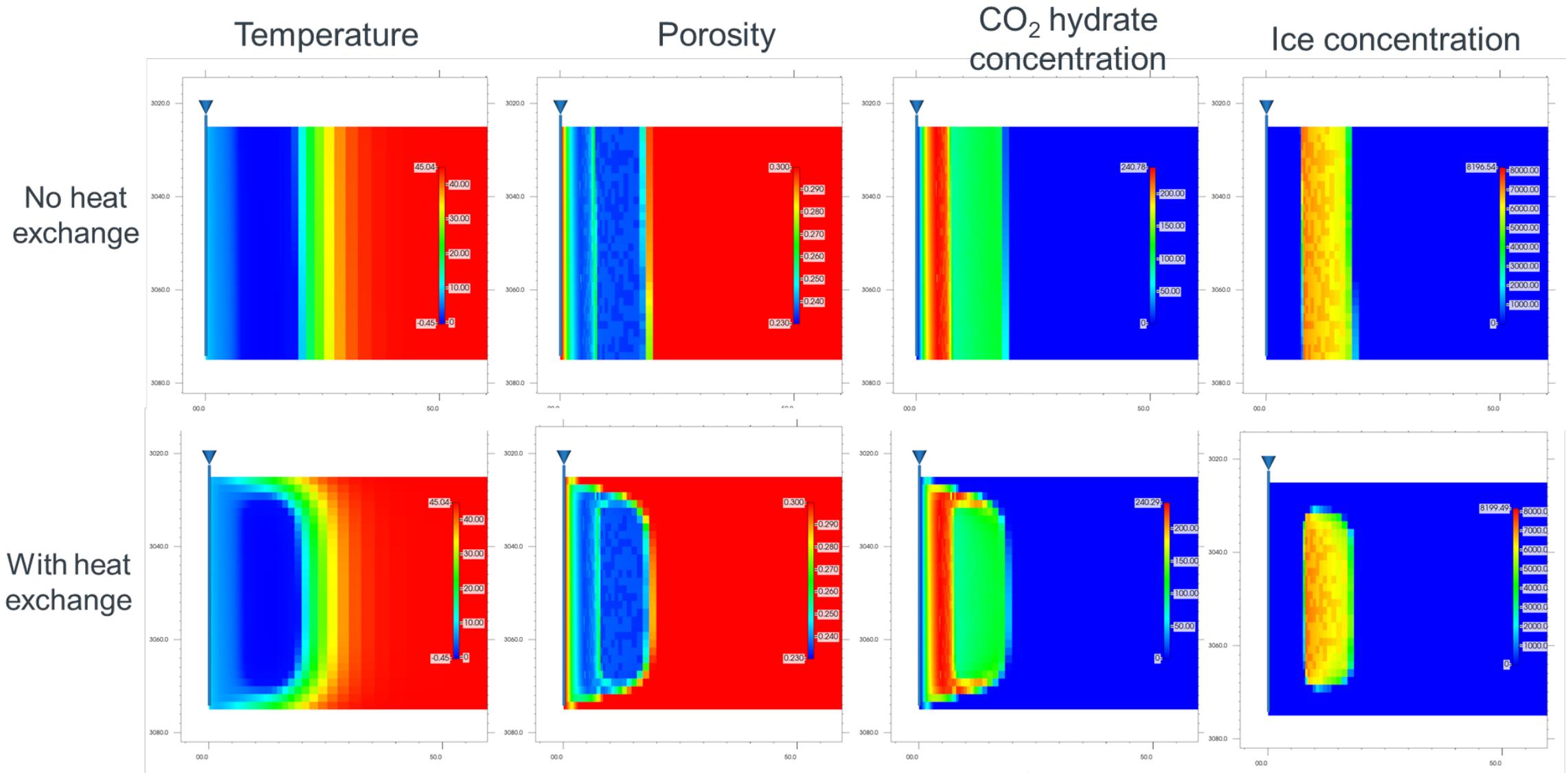
# Perm. reduction due to hydrate formation (1 year)

— No perm reduction  
 - - Perm reduction



Perm reduction leads to higher pressure drawdown and more JT cooling

# Impact of heat exchange for 3D case (1 year)

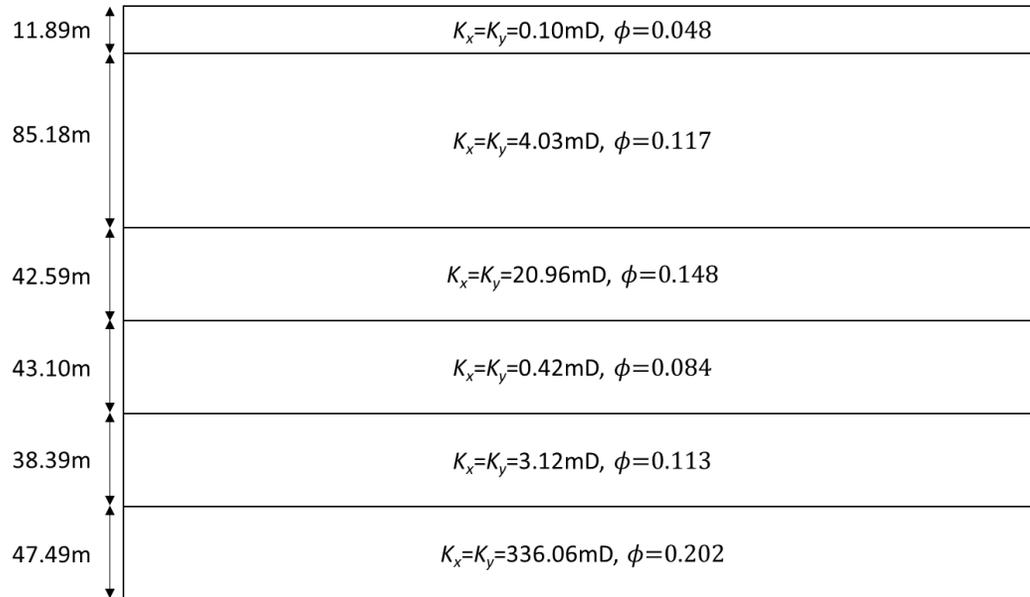


Heat exchange cannot mitigate hydrate formation

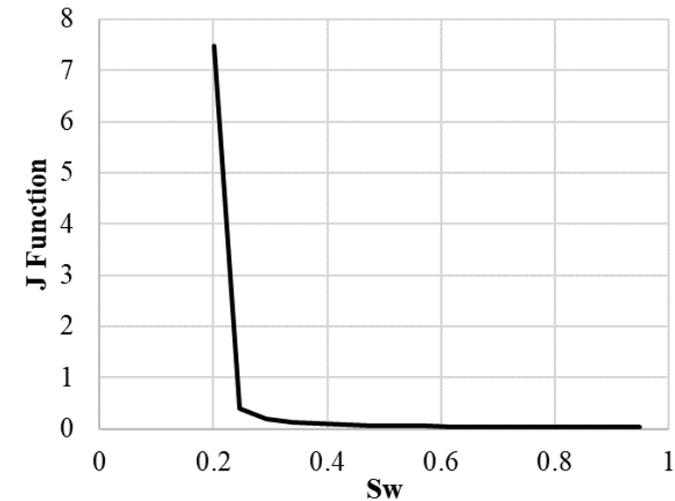
# Multilayered Reservoir

“Indina et al., On The Significance of Hydrate Formation/Dissociation during CO<sub>2</sub> Injection in Depleted Gas Reservoirs. 2024 Oman Petroleum & Energy Show (OPES), SPE-218550-MS.”

- 100x1x6 radial grid with refinement
- Each layer has different porosity and permeability
- Reservoir initially filled with water and methane
- Initial reservoir temperature: 135°C

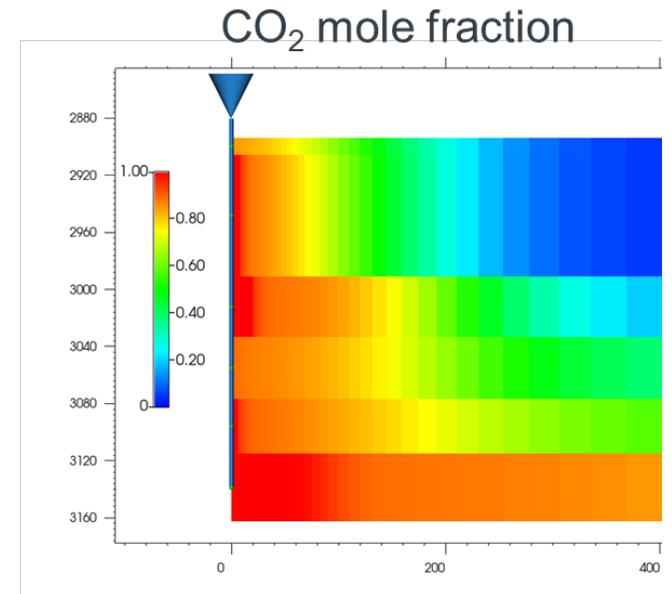
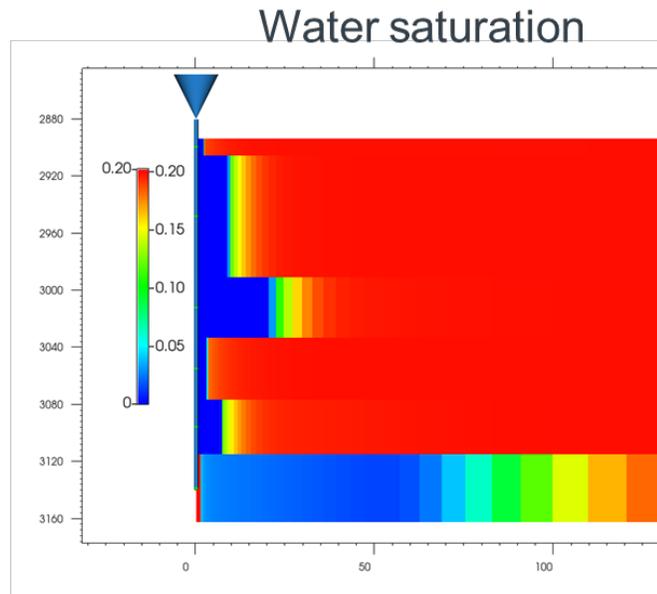
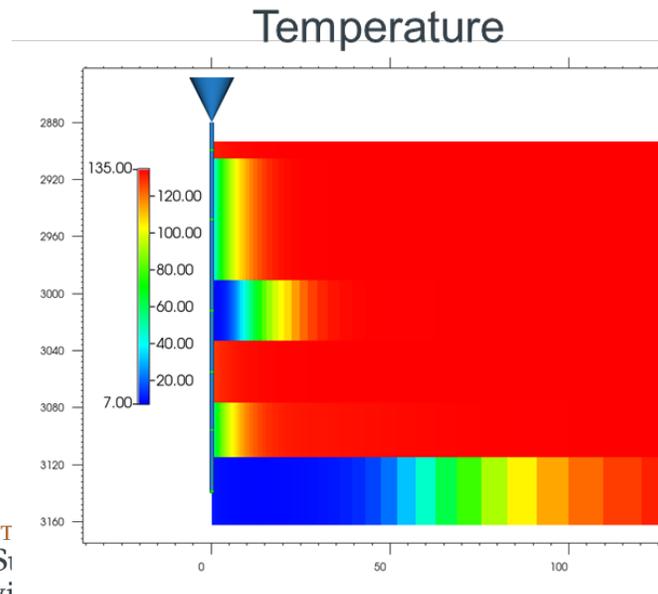
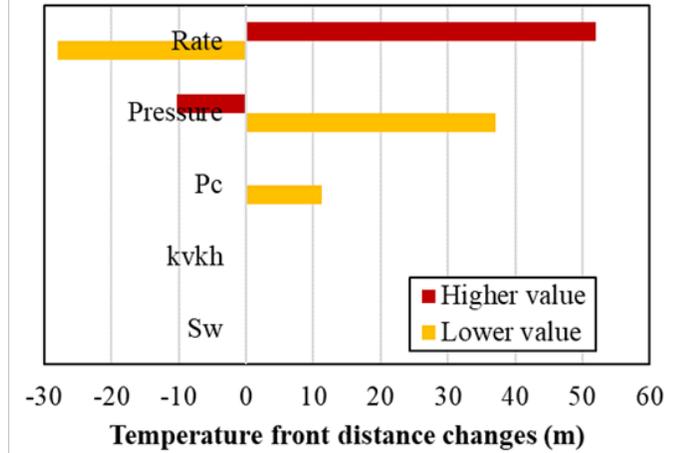
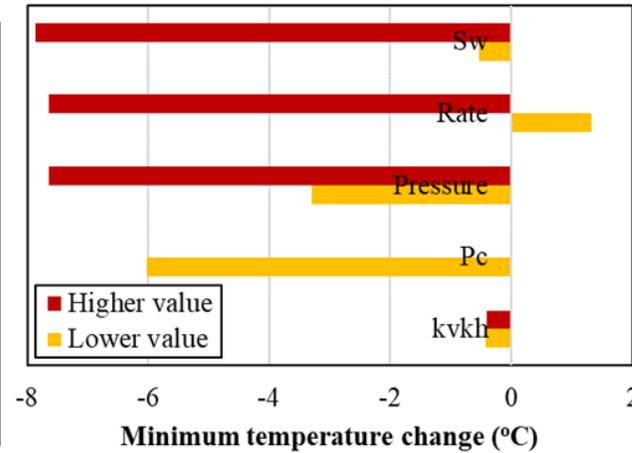


| Properties               | Value          | Sensitivity    |
|--------------------------|----------------|----------------|
| Initial water saturation | 0.2            | 0.15 and 0.3   |
| Injection temperature    | 10 °C          | -              |
| Initial pressure         | 2.5 MPa        | 1 and 4 Mpa    |
| Injection rate           | 1 MMTA         | 0.5 and 2 MMTA |
| Kv/Kh                    | 0.1            | 0.5 and 1      |
| Capillary pressure       | Not considered | J-function     |



# Results after 1 year of simulation

- Higher saturation = More hydrates and higher cooling
- Increase in rate = Increase pressure drawdown
- Lower initial pressure = Higher JT cooling
- Higher initial pressure = Higher hydrate equilibrium temperature



# Summary and Conclusions

- Just like in wellbore and pipeline, hydrate formation is also a risk in porous media.
- The Joule-Thomson effect can cool CO<sub>2</sub> to hydrate and freezing conditions even in high-temperature reservoirs.
- The heat gain from surrounding formation, heat of hydrate formation, and water dry-out did not prevent hydrate formation.
- Permeability, injection rate, initial reservoir pressure, and injection temperature all play a critical role in the formation of hydrate.

# Acknowledgement

- PI's: Mojdeh Delshad, Kamy Sepehrnoori, and Rouhi Farajzadeh
- **Students:** Vincent Indina, Kenta Yamada, and Atharva Kalamkar
- Financial support: Shell

