ACADEMIC SEMINAR

Desalination by Hydrate Crystallization Process Engineering

Hanoi, 05-2023

Outlines

1. Contexts and Objectives
2. Hydrate Backgrounds & Applications
3. Desalination by Hydrate Engineering
4. Apparatus-Result-Discussion
5. Conclusions
6. Acknowledgements

1. Contexts and Objectives

- Water is a vital and indispensable resource for sustainable and human development.

- Natural clean water is increasingly scarce due to population growth, urbanization, and climate change. Today, about 1.2 billion people cannot access clean and safe water.

- Besides, salty waste water is being needed to treat with salt removal.

➡ **Therefore, water desalination is becoming more important.**

1. Contexts and Objectives

- Currently, there are several methods of salts removal from seawater, such as: thermal distillation, cold freezing, reverse osmosis (RO), etc.

- However, these processes consume a lot of energy, increasing greenhouse gas emissions. A typical seawater desalination is reverse osmosis (RO). This process requires a high energy consumption and a high cost of equipment and regeneration of membrane materials used.

- Currently, a hydrate crystallization process is being applied to seawater desalination.

➡ **This study will focus on kinetics of hydrate-based desalination (HBD) process.**

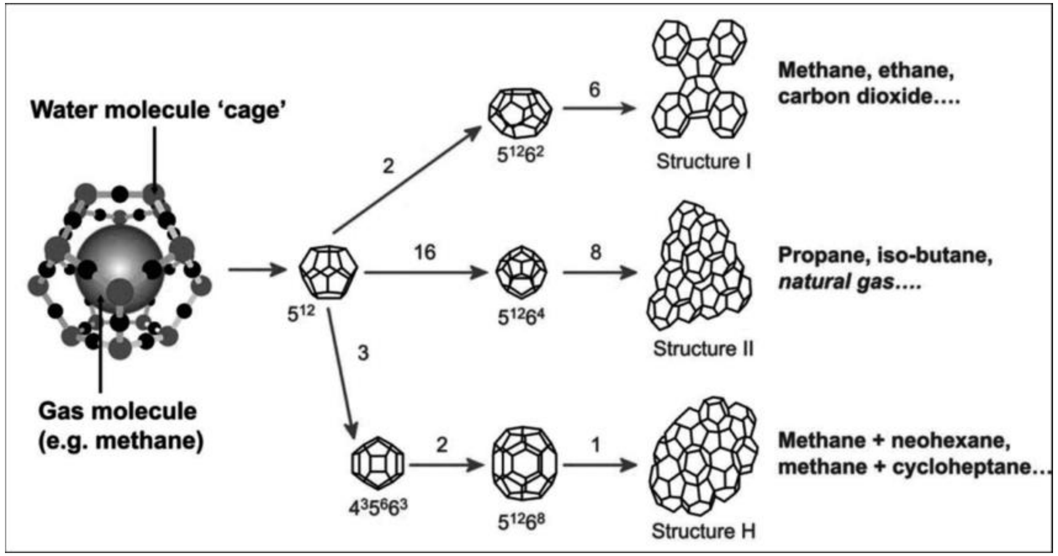
Additionally, this work will seek the way to enhance the effectiveness of HBD process.

2. Hydrate Backgrounds & Applications

- Hydrate is a solid compound formed by water and guest molecule (hydrocarbons, H_2S, CO_2, H_2, N_2, O_2, etc.) at low temperature and possibly at high pressure.

- Applications of hydrates: methane hydrate resource as a huge future fuel, gas storage and separation, water treatment, flow assurance, etc.

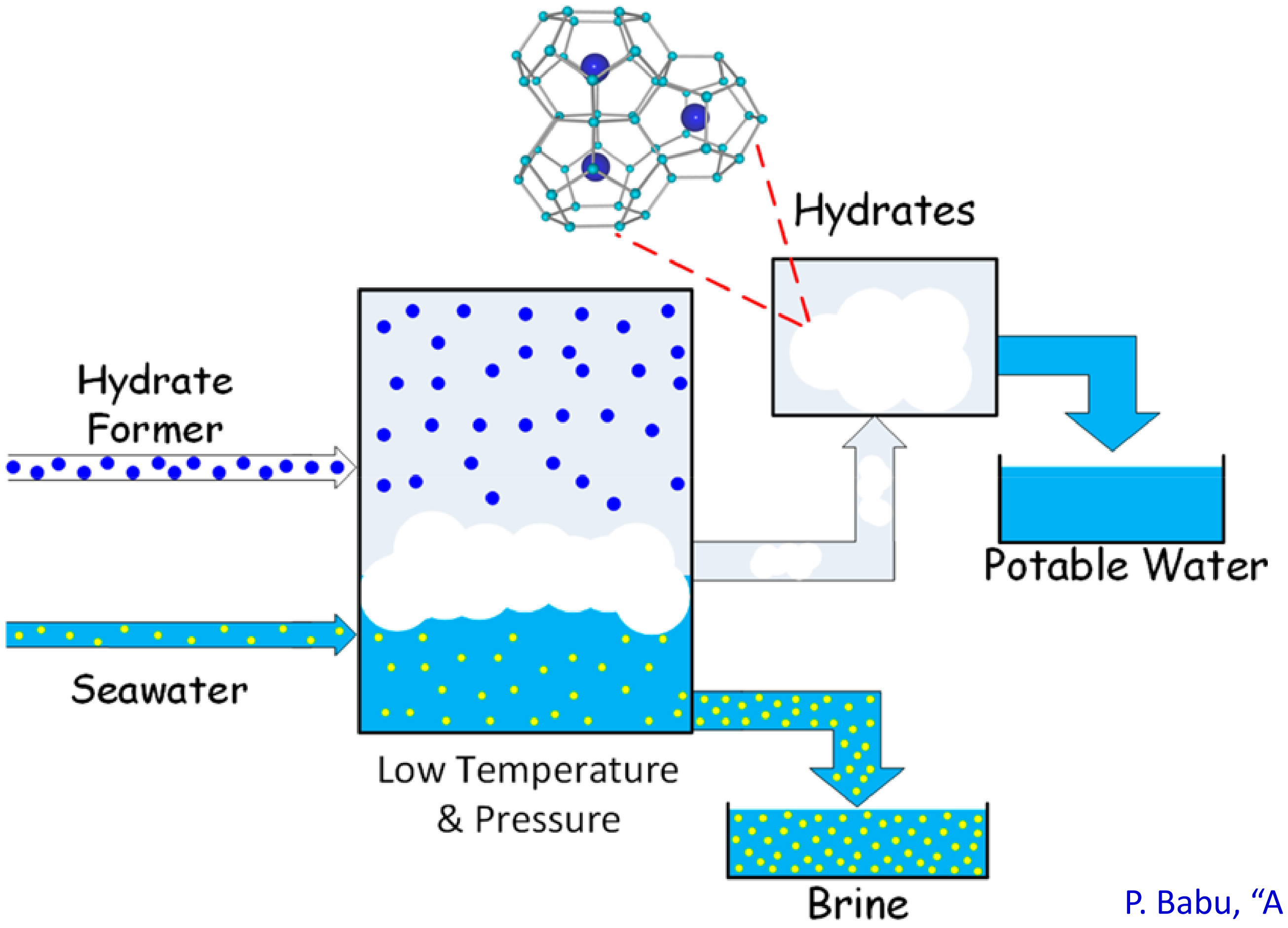
https://www.netl.doe.gov



Hydrate structures (from Center for Gas Hydrate Research – Heriot Watt)

2. Hydrate Backgrounds & Applications

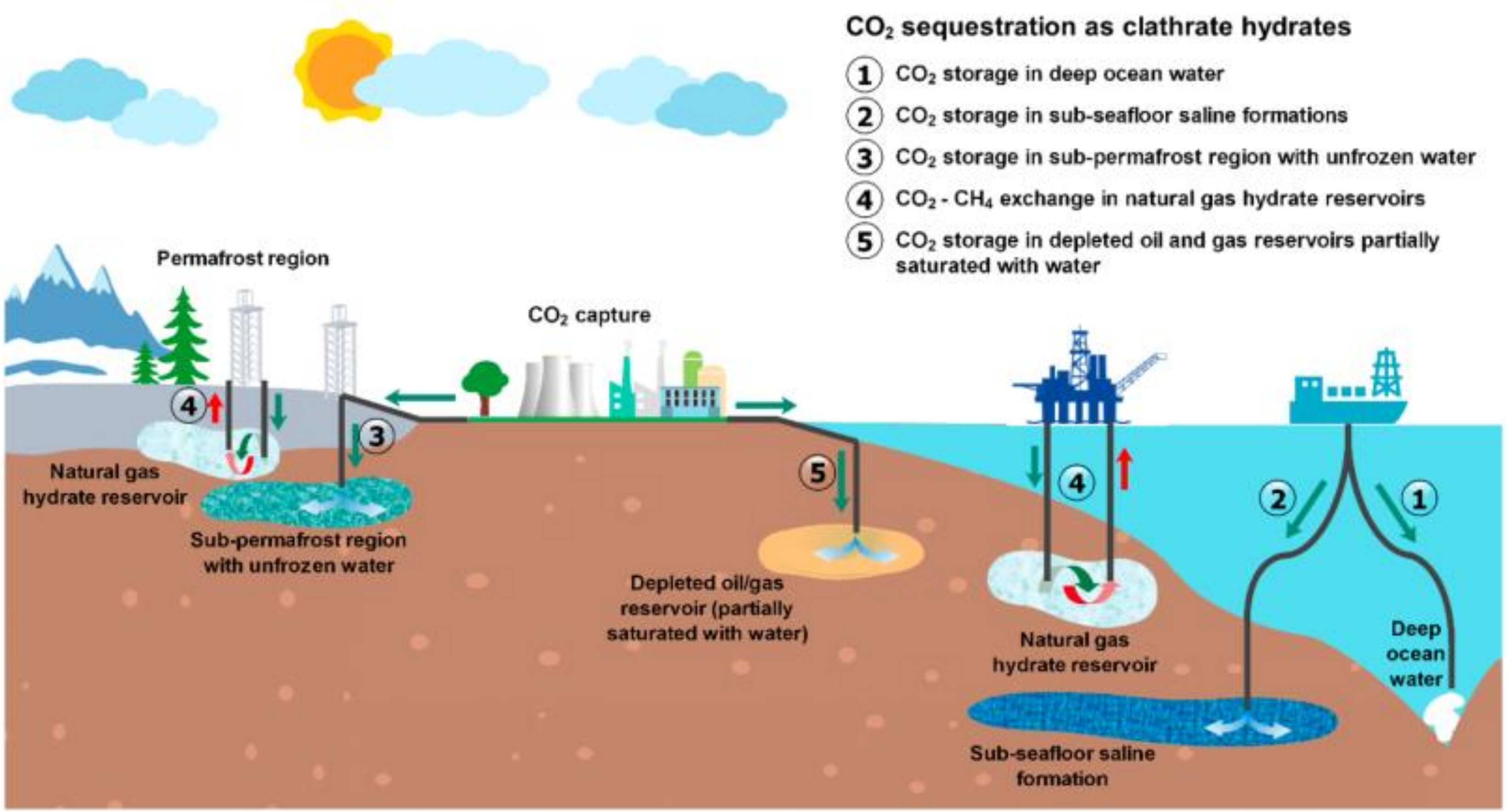
Water treatments (waste water or desalination)



P. Babu, "A review of the hydrate based gas separation (HBGS) process for carbon dioxide pre-combustion capture," *Energy*, 2015

2. Hydrate Backgrounds & Applications

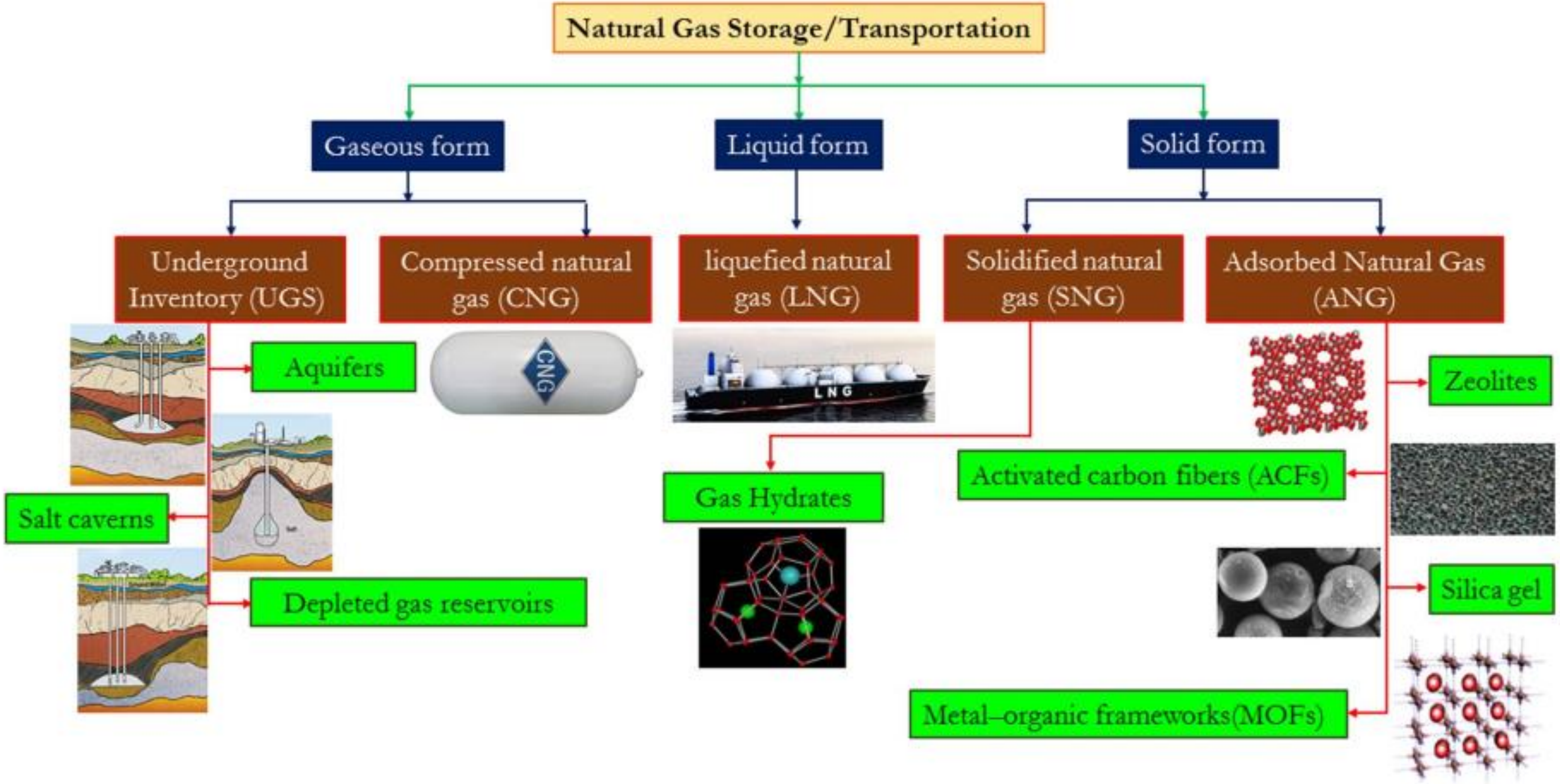
CO_2 capture/storage/sequestration



Junjie Zheng, Zheng Rong Chong, M. Fahed Qureshi, and Praveen Linga*. **Carbon Dioxide Sequestration via Gas Hydrates: A Potential Pathway toward Decarbonization**, *Energy Fuels* 2020

2. Hydrate Backgrounds & Applications

Gas separation & storage (natural gas storage & transport)



Pathways for natural gas storage and transportation (Images on UGS obtained from http://www.energyinfrastructure.org/energy-101/natural-gas-storage).

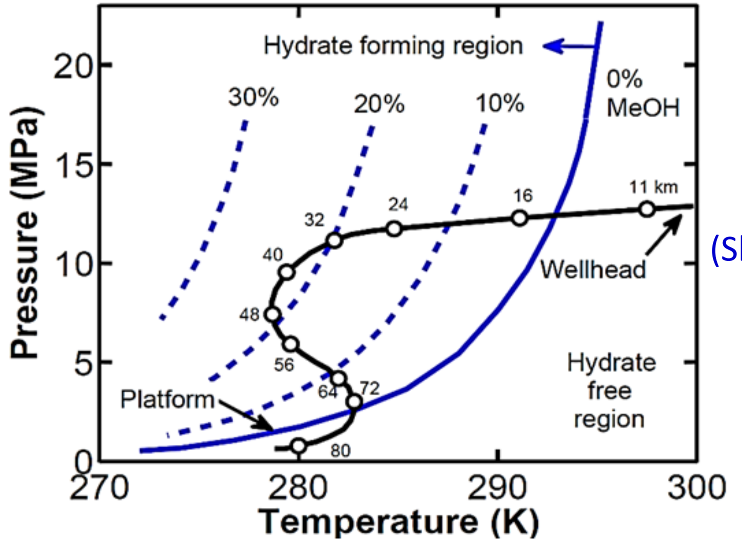
2. Hydrate Backgrounds & Applications

Flow assurance

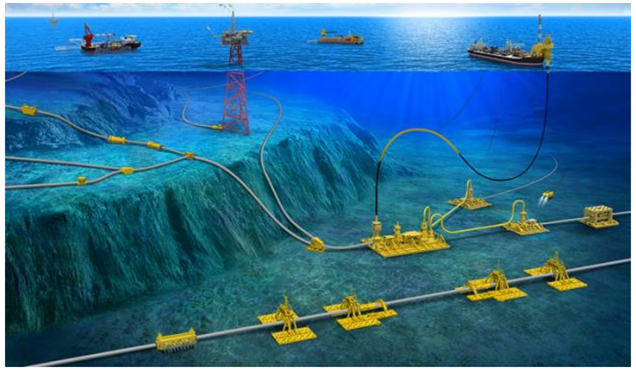
Mines Saint-Étienne

Une école de l'IMT

- ❑ **Methane hydrate formed by water and gas at 4°C and 80 bar.**
- ❑ **Methane hydrate can cause plugs in oil pipelines (costly to prevent, remove and induce safety risks).**

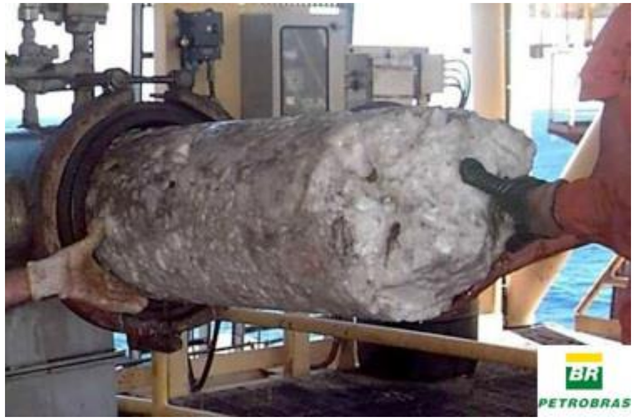


(Sloan and Koh, 2008)



(Subsea pipelines - Oilstates, 2017)

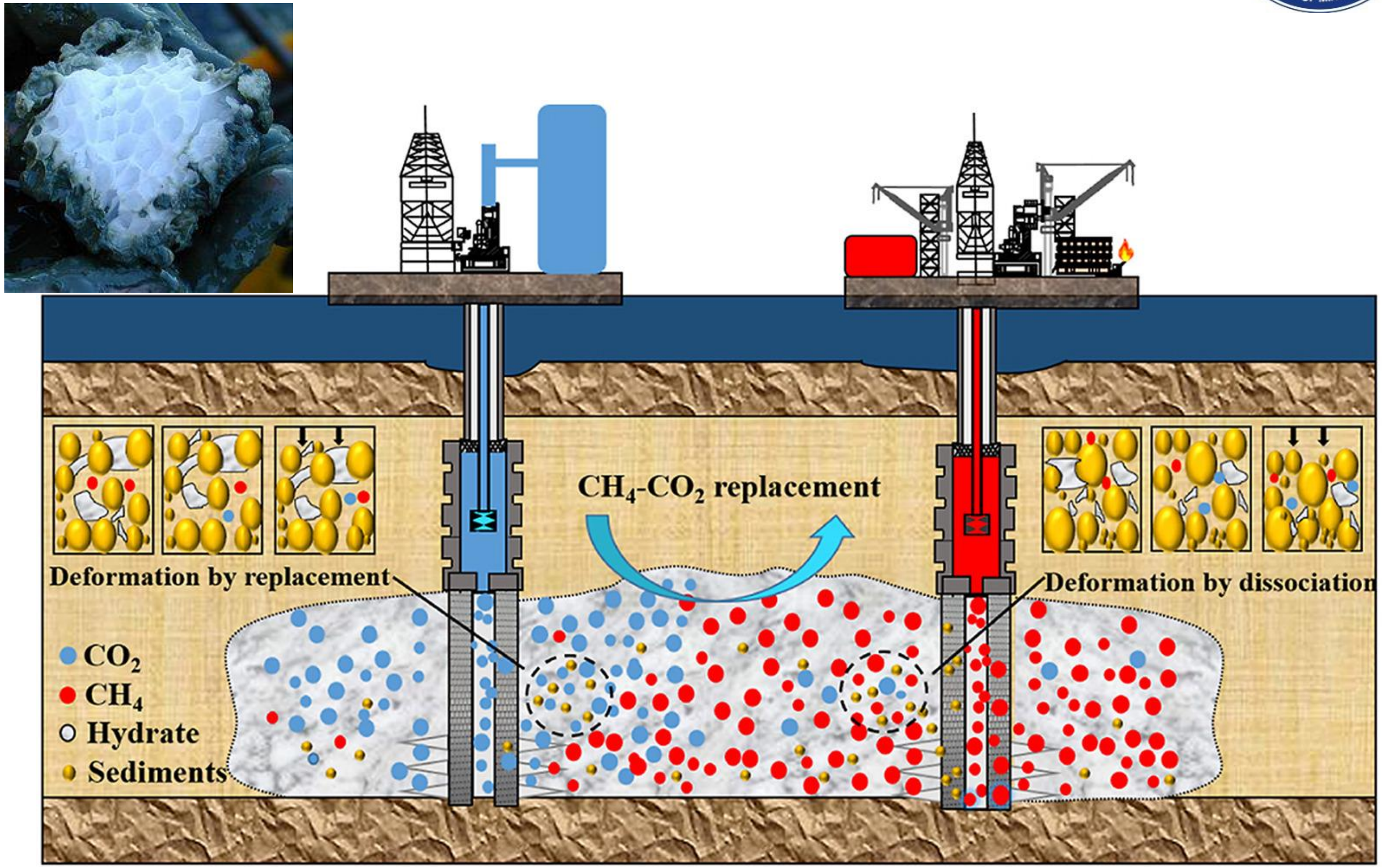
- ❑ **Oil and gas fields gradually become mature, leading to an increase in water production (or high water cut).**
- ❑ **Anti-Agglomerant-Low Dosage Hydrate Inhibitors (AA-LDHIs) are the best candidates to prevent PLUG compared to Thermodynamic Inhibitors (THIs) and Kinetic Hydrate Inhibitors (KHIs).**



(Hydrate recovered at slug catcher-Petrobras)

2. Hydrate Backgrounds & Applications

Natural gas hydrate recovery



Tingting_Luo et al., Deformation behaviors of hydrate-bearing silty sediments during CH_4–CO_2 replacement, [Journal of Petroleum Science and Engineering](), 2022

3. Desalination by Hydrate Engineering

Une école de l'IMT

- In this process, the pure water molecule creates a framework around the guest molecules (gas or/and liquid) that creates hydrate crystals (solids). This way separates the pure water from dissolved ions (salts) in the salty water.

- These solid hydrate particles are then collected and dissociated, producing (separating) pure water and (gas or/and liquid) guest molecules which are recycled to desalination process.

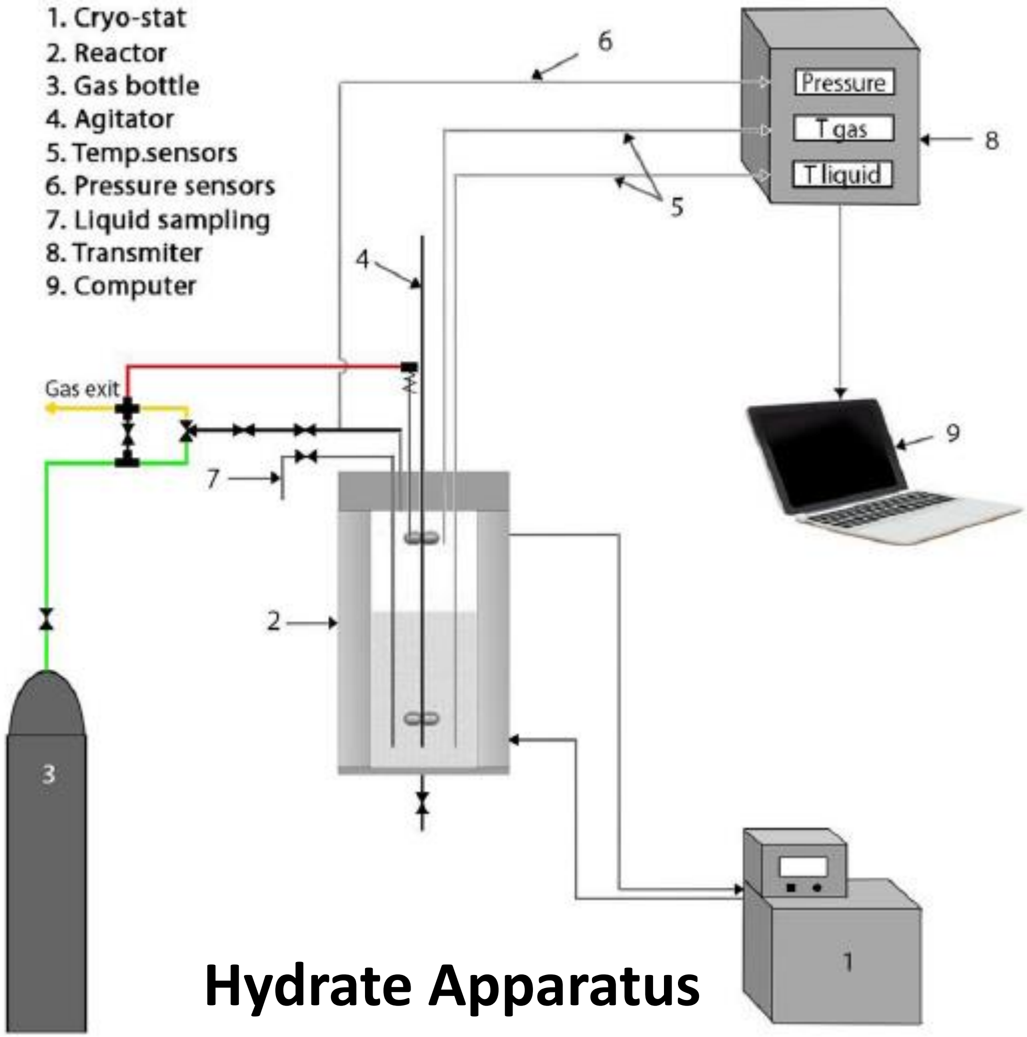
- The advantages of salts removed by hydrate process engineering are (1) low energy cost (and can utilize cold energy from other processes), (2) applicable to high salty solutions, (3) high capacity, (4) environmentally friendly (no secondary processes causing environmental pollution and additives/hydrate promoters are regenerated), (5) simple technique and (6) using cheap and available materials.

4. Apparatus-Result-Discussion

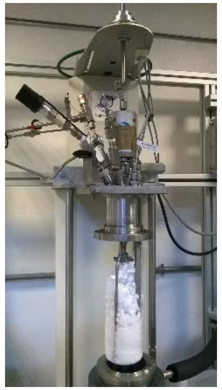
- Cyclopentane (CP) is used as hydrate former due to:
  - (1) high salt separation efficiency
  - (2) can separate CP from fresh water after removing salt
  - (3) low energy cost
  - (4) cheap, abundant, readily available process materials
  - (5) no pollution to the environment
- In this research, CP-hydrates and CP-CO_2 hydrates are investigated for desalination with thermodynamics and kinetics.

4. Apparatus-Result-Discussion

Hydrate Thermodynamics & Kinetics

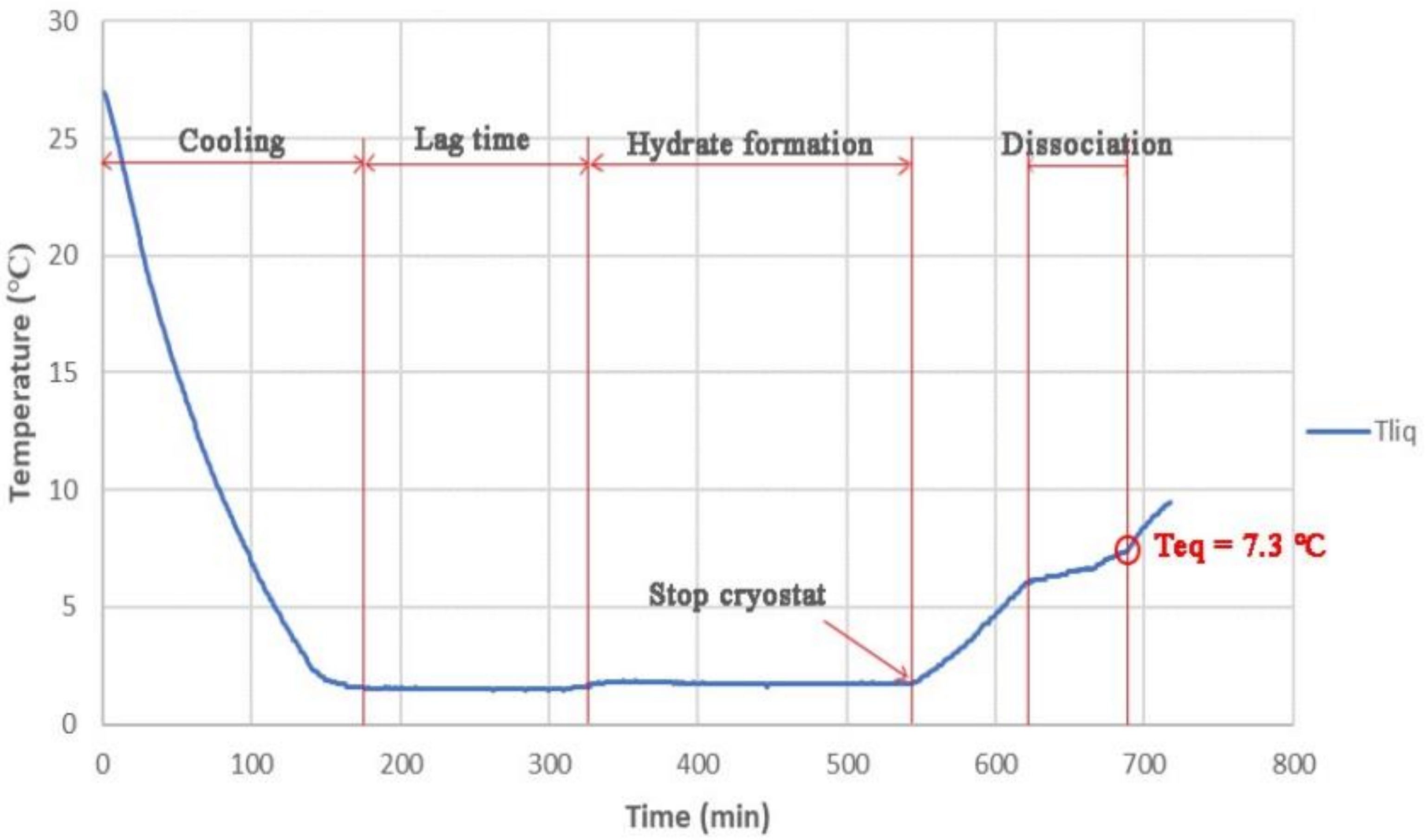


Hydrate Apparatus



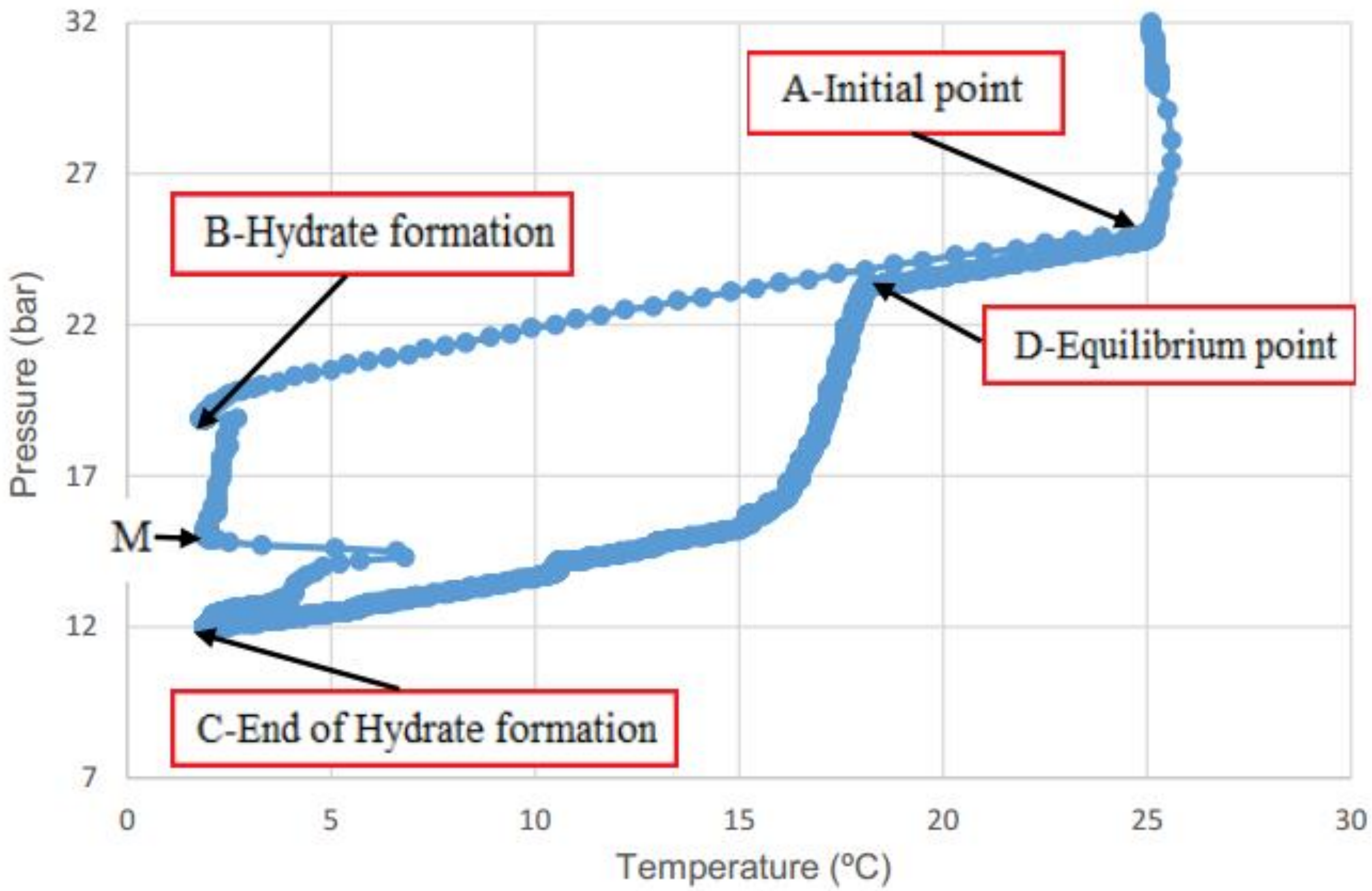
4. Apparatus-Result-Discussion

CP-Hydrate Thermodynamics (Equilibrium-Modelling) & Kinetics



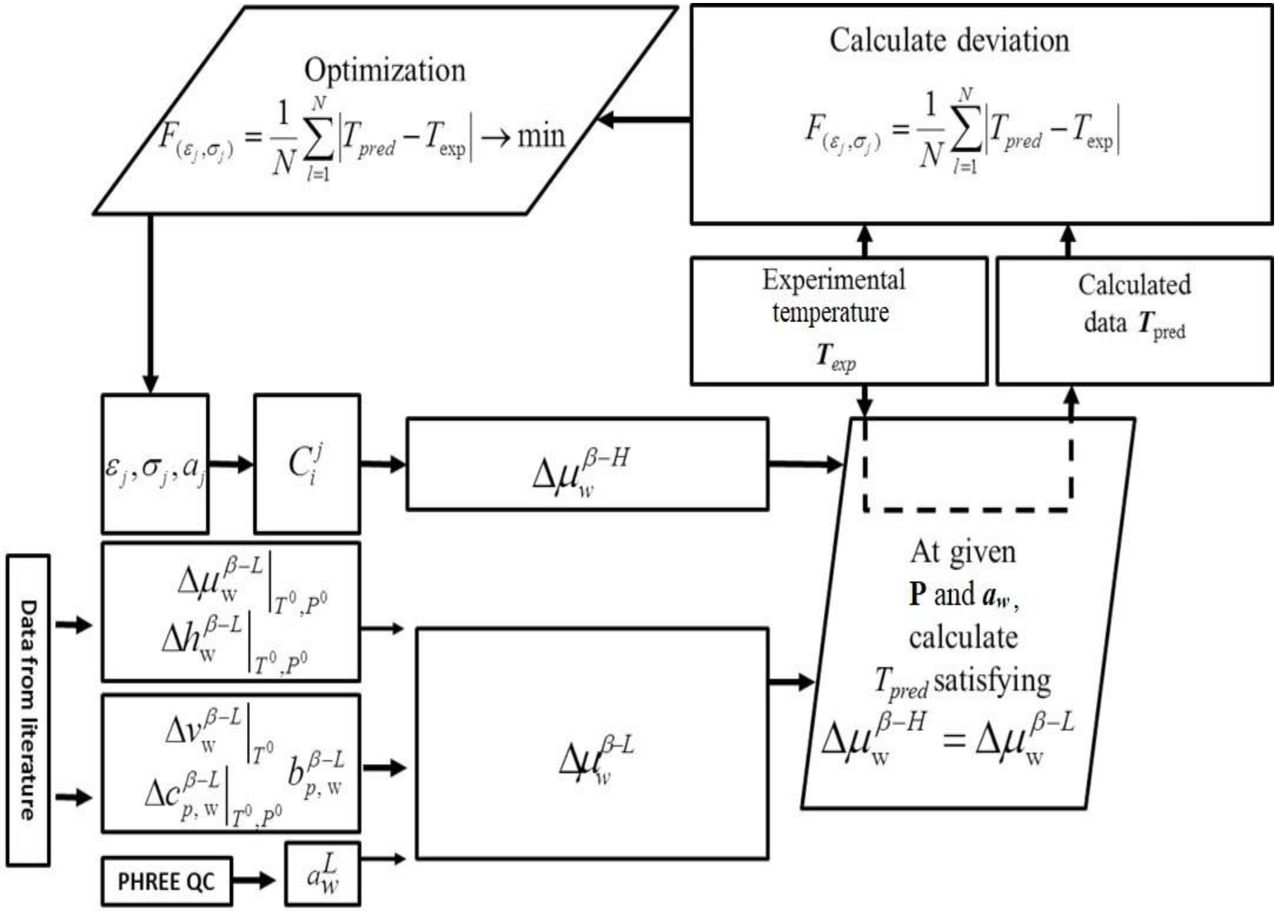
4. Apparatus-Result-Discussion

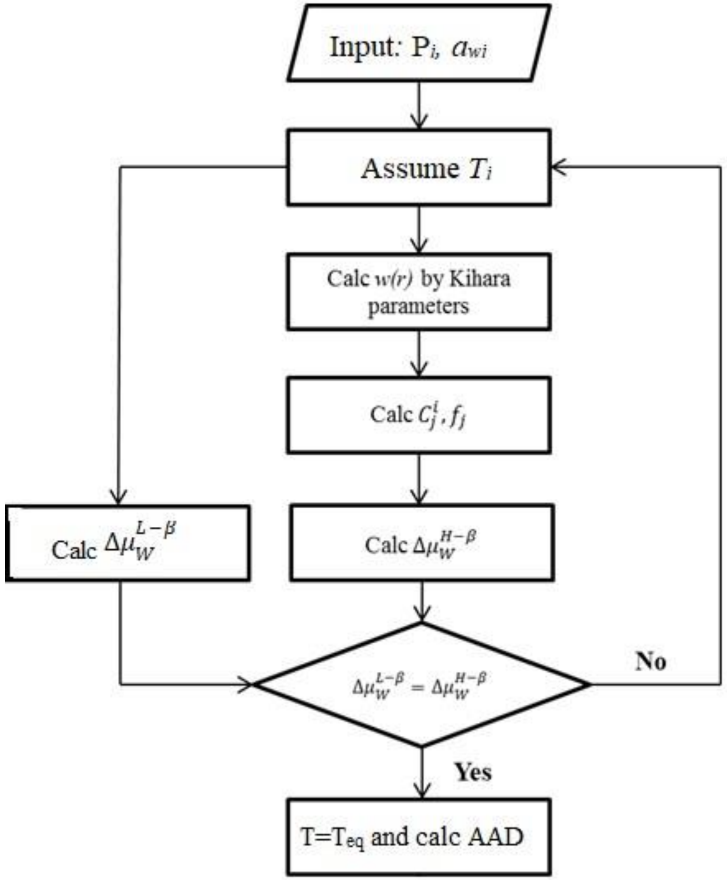
CP-CO_2-Hydrate Thermodynamics (Equilibrium & Modelling)



4. Apparatus-Result-Discussion

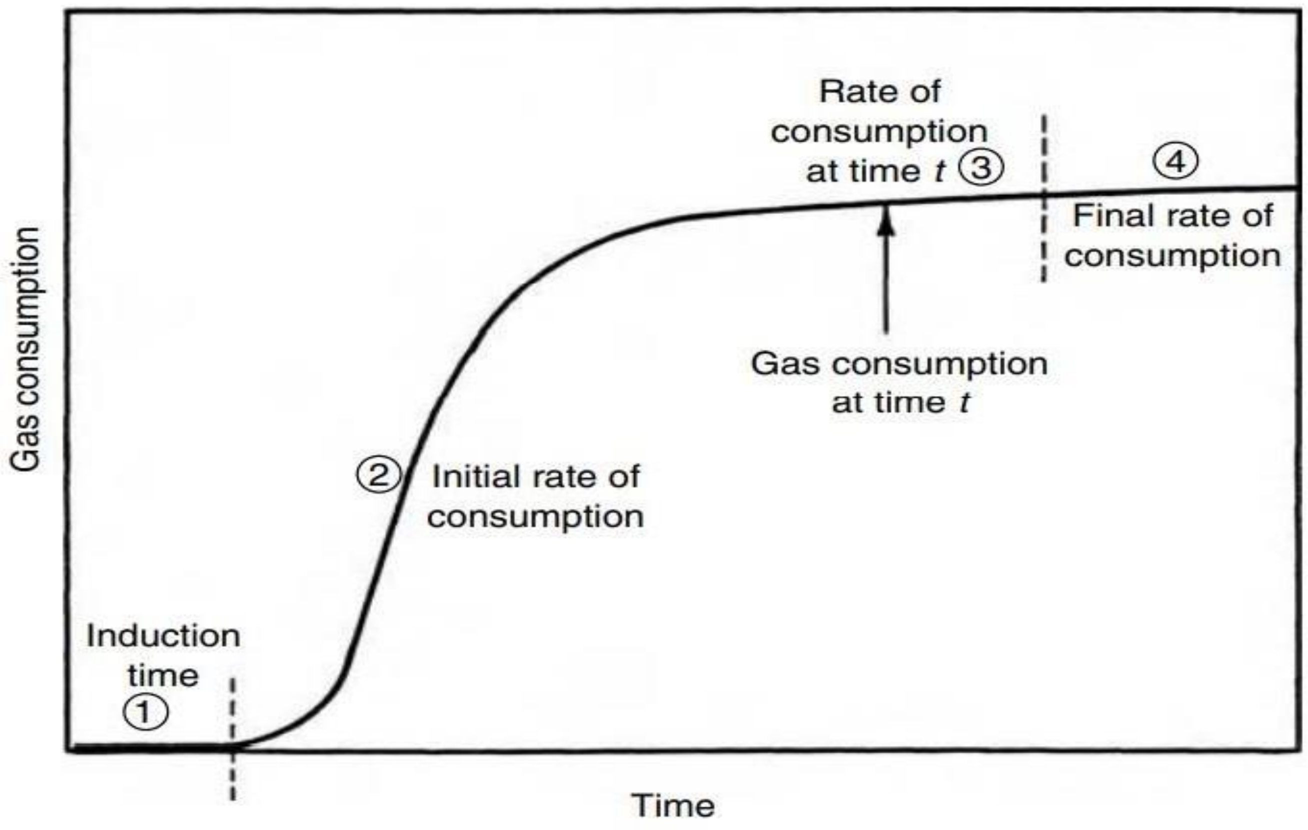
CP-CO_2-Hydrate Thermodynamics (Equilibrium & Modelling)





4. Apparatus-Result-Discussion

CP-CO_2-Hydrate Kinetics



Sloan, E.; Koh, C.A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; Taylor and Francis Group: Abingdon, UK, 2008

4. Apparatus-Result-Discussion

CP hydrates (Thermodynamics & Kinetics) - Experimental Results

1. Finish experiments with Thermodynamics of CP hydrates without/with NaBr (0; 3.5; 5; 10; 15; 20 wt.%) rpm=400
2. Finish experiments with Thermodynamics of CP hydrates without/with KBr (0; 3.5; 5; 10; 15; 20 wt.%) rpm=350; 400 and 500
3. Finish experiments with Thermodynamics of CP hydrates without/with Na2SO4 (0; 3.5; 5; 10; 15; 20 wt.%) rpm=400 and 500
4. Finish experiments with Thermodynamics of CP hydrates without/with K2SO4 (0; 3.5; 5; 7.5; 10 wt.%) rpm=400 and 500
5. Finish experiments with Kinetics of CP hydrates with 3-5%wt NaCl (effects of temperature, agitation speed, CP amount)

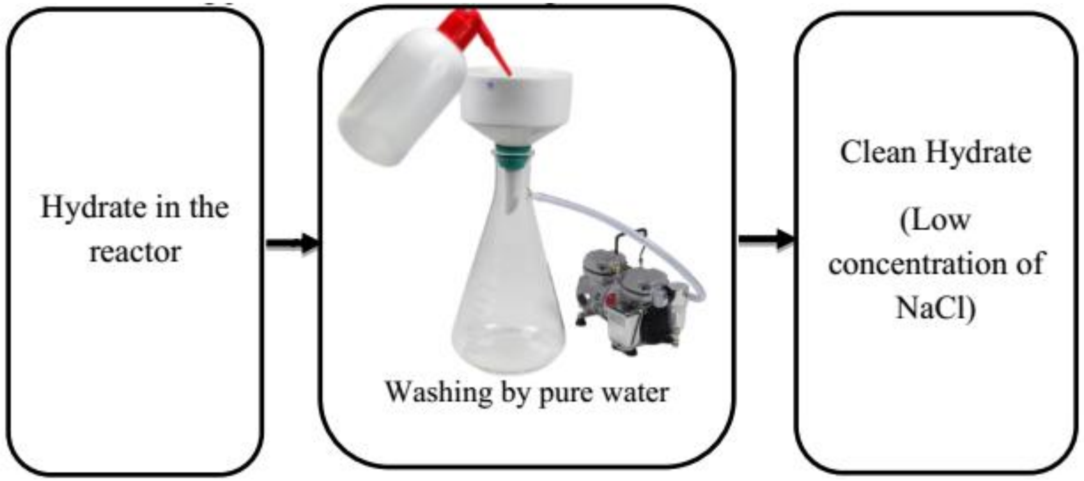
4. Apparatus-Result-Discussion

$CP\text{-}CO_2$ hydrates (Thermodynamics & Kinetics) - Experimental Results

1. Finish experiments with Thermodynamics & Kinetics of CP-CO2 hydrate without/with NaBr (P=27; 32; 37 bar)
2. Finish experiments with Thermodynamics & Kinetics of CP-CO2 hydrate without/with KBr (P=27; 32; 37 bar)
3. Finish experiments with Thermodynamics & Kinetics of CP-CO2 hydrate without/with Na2SO4 (P=27; 32; 37 bar)
4. Finish experiments with Thermodynamics & Kinetics of CP-CO2 hydrate without/with K2SO4 (P=27; 32; 37 bar)
5. Finish experiments with Kinetics of $CP\text{-}CO_2$ hydrates with 3.5%wt NaCl (effects of temperature, pressure, agitation speed, CP amount)

4. Apparatus-Result-Discussion

Enhance desalination using $CP\text{-}CO_2$ hydrate with 3.5%wt NaCl



STT	Phase	Position	Washing (time)	% NaCl before	%NaCl after hydrate formation and washing
1	Liquid	Valve (Bottom)	-	3.5	4.11
2	Hydrate	Inside (Bottom)	-	3.5	3.43
3	Hydrate	Inside (Agitator)	3	3.5	0.13
4	Hydrate	Inside (Wall)	5	3.5	0.082
5	Hydrate	Inside (Bottom)	3	3.5	0.37

5. Conclusions

1. Hydrate is a solid compound (like ice or snow) formed by water and guest molecule (hydrocarbons, H_2S, CO_2, H_2, N_2, O_2, etc.) at low temperature and possibly at high pressure.
2. Applications of hydrates: methane hydrate resource as a huge future fuel, gas storage and separation, water treatment, flow assurance, etc.
3. Currently, a hydrate crystallization process is being applied to seawater desalination.
4. Cyclopentane (CP) is used as hydrate former due to: (1) high salt separation efficiency; (2) can separate CP from fresh water after removing salt; (3) low energy cost; (4) cheap, abundant, readily available process materials; (5) no pollution to the environment.
5. **In this research, CP-hydrates and CP-CO_2 hydrates are investigated for desalination with thermodynamics and kinetics. It is reported that hydrate crystallization process is highly potential for seawater desalination.**

6. Acknowledgements

1. SPIN Centre, Saint-Etienne School of Mines (EMSE)
2. International Co-operation Office (EMSE and HUMG)
3. Faculty of Petroleum and Energy, Hanoi University of Mining and Geology (HUMG)
4. Oil Refining and Petrochemical Department (HUMG)
5. Advanced Program in Chemical Engineering (HUMG)