DESALINATION OF CONTAMINATED WATER VIA CLATHRATE HYDRATES

Russell School of Chemical Engineering, University of Tulsa

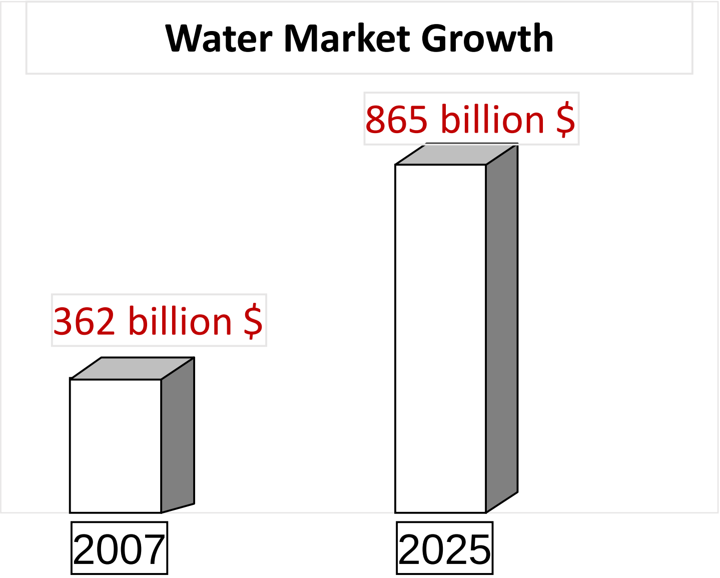
7 Oct 2019

Daraboina Research Group

Outline

- Current Water Situation
- Existing Desalination Technologies
- Desalination via Clathrate Hydrate
- Challenges with Desalination via Clathrate Hydrate
- Thermodynamics
- Kinetics
- Conclusion and Recommendations

Current Water Situation



< Global Water Intelligence, 2008 >

Sea Water

Abundant resource for fresh water on earth

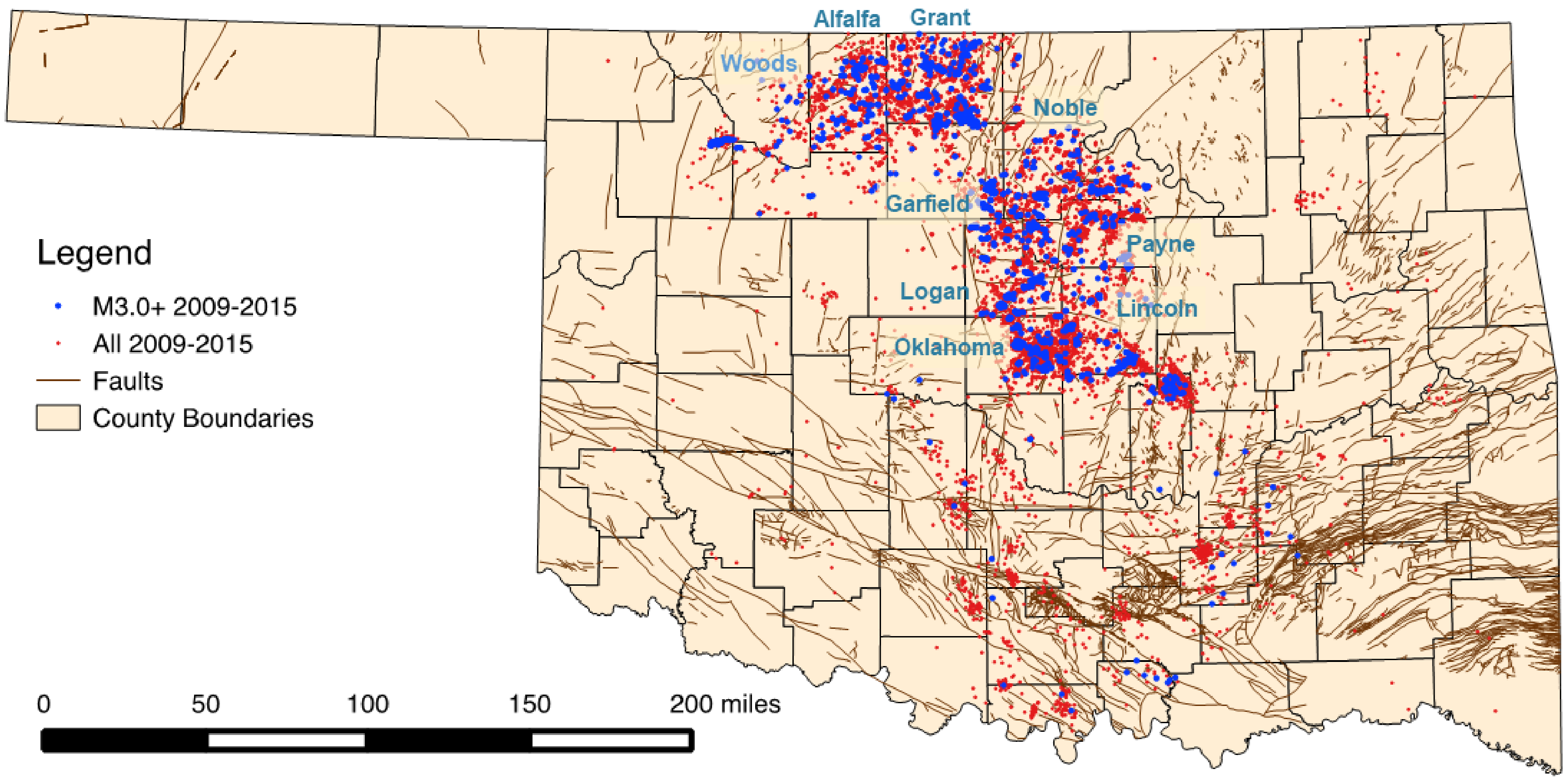
Daraboina Research Group

Major Water using industries

- **Oil and Gas**
- Petrochemical
- Power
- Food processing
- Pharmaceutical
- Microelectronics
- Pulp and paper
- Mining

Produced water (PW)

- The water found in the same formations as oil and gas and is a byproduct of oil and gas exploration and production
- PW generated throughout the World is up to 39.5 million m^3 per day
- 9.2 million m^3/day of produced water in US alone
- Total dissolved solids of PW can be up to 300,000 mg/L
- Treated PW can be reused for
  - irrigation,
  - livestock watering
  - aquifer storage
  - municipal and industrial uses



Jeremy Boak., “Oklahoma Earthquakes and Injection of Produced Water” Oklahoma Geological Survey, 2016

Existing Desalination Technologies

Desalination

- **Distillation (MSF)**
  - High energy cost;
  - Corrosion issues;
- **Membrane (RO)**
  - Requires pretreatment;
  - Sensitive to impurities;
  - High Maintenance Cost;
  - 37-50% Water Recovery;
- **Freeze Distillation (FD)**
  - Energy intensive;
  - 20% Water Recovery;
  - Brine-crystal separation;

Limitations of Existing Techniques

- Sensitive to salt concentration and impurities
- Energy intensive
- Low water recovery

→ Disruptive – Innovative Technologies

DRG Daraboina Research Group

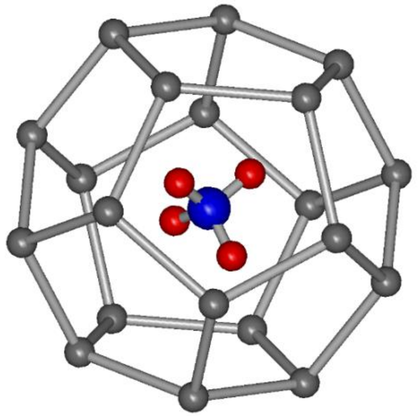
Disruptive – Innovative Technology

- **Cost effective**
- **Environmentally friendly**
- **Low in energy consumption**
- **Raw material availability**
- **High recovery**
- **Sustainable**

Can hydrate based desalination be the answer?

Gas hydrates are crystals like ice

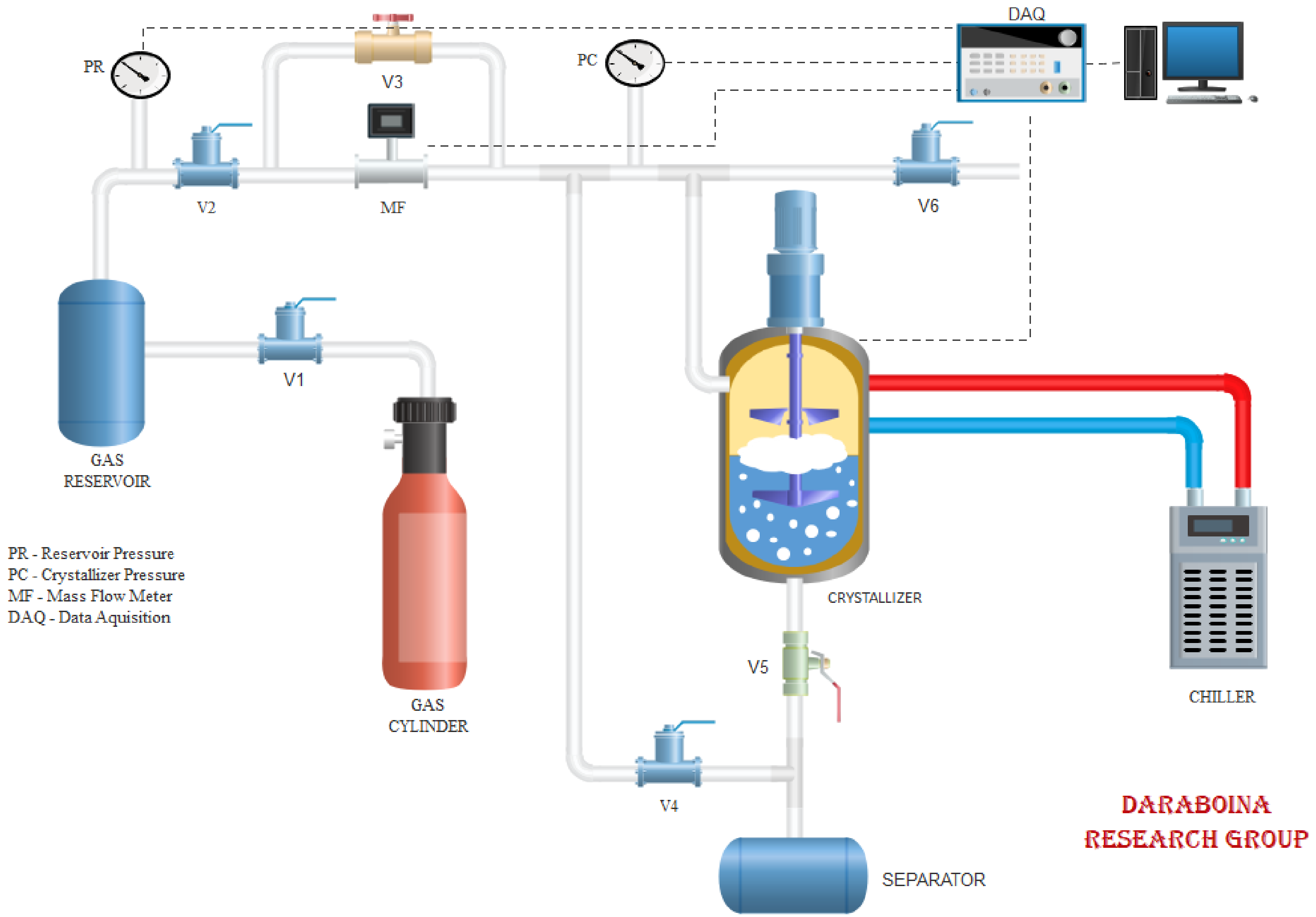
- Non-stoichiometric crystalline compounds
- Formed by enclathration of guest molecules by cages formed by water molecules
- Guest molecule may be H_2 , CO_2, Hydrocarbons, N_2 etc.
- Hydrates are relevant to flow assurance, energy recovery and innovative applications



Molecular view

Naked eye view

Desalination via Clathrate Hydrate



What are the advantages?

- ✓ No reaction, easy to recover water
- ✓ Salt ions and impurities get rejected
- ✓ Treat up to eutectic salinity **230000**
- ✓ Hydrates consist of 85% water!

What are the challenges?

- ➢ Slow rate of gas hydrate formation
- ➢ Separation of gas hydrate from brine
- ➢ Refrigeration requirement

DRG Daraboina Research Group

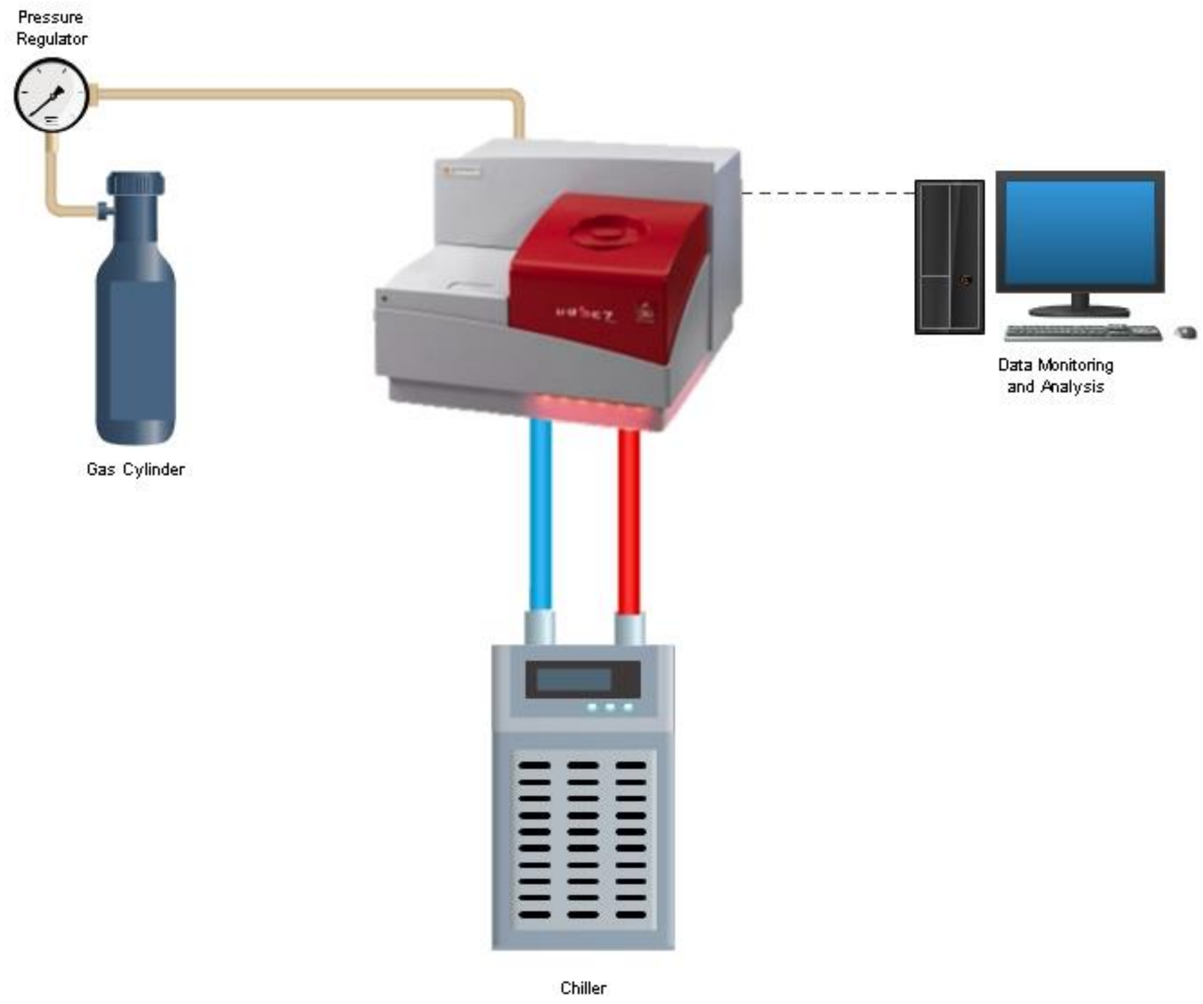
Challenges

- Refrigeration requirement -----> Thermodynamics -----> Identification of suitable hydrate former to operate at higher temperature
- Slow rate of gas hydrate formation -----> Reactor design and Suitable hydrate former
- Separation of gas hydrate from brine -----> Reactor design

Our capabilities - Scalability

µDSC	Small scale Kinetic Setup	Prototype Setup
Volume = 1 ml	**Volume = 100 ml**	**Volume = 4 L**
Thermodynamics	**Thermodynamics and Kinetics measurement**	**Kinetics measurement**
No separation of hydrate crystals	**No separation of hydrate crystals**	**Separation of hydrate crystals**

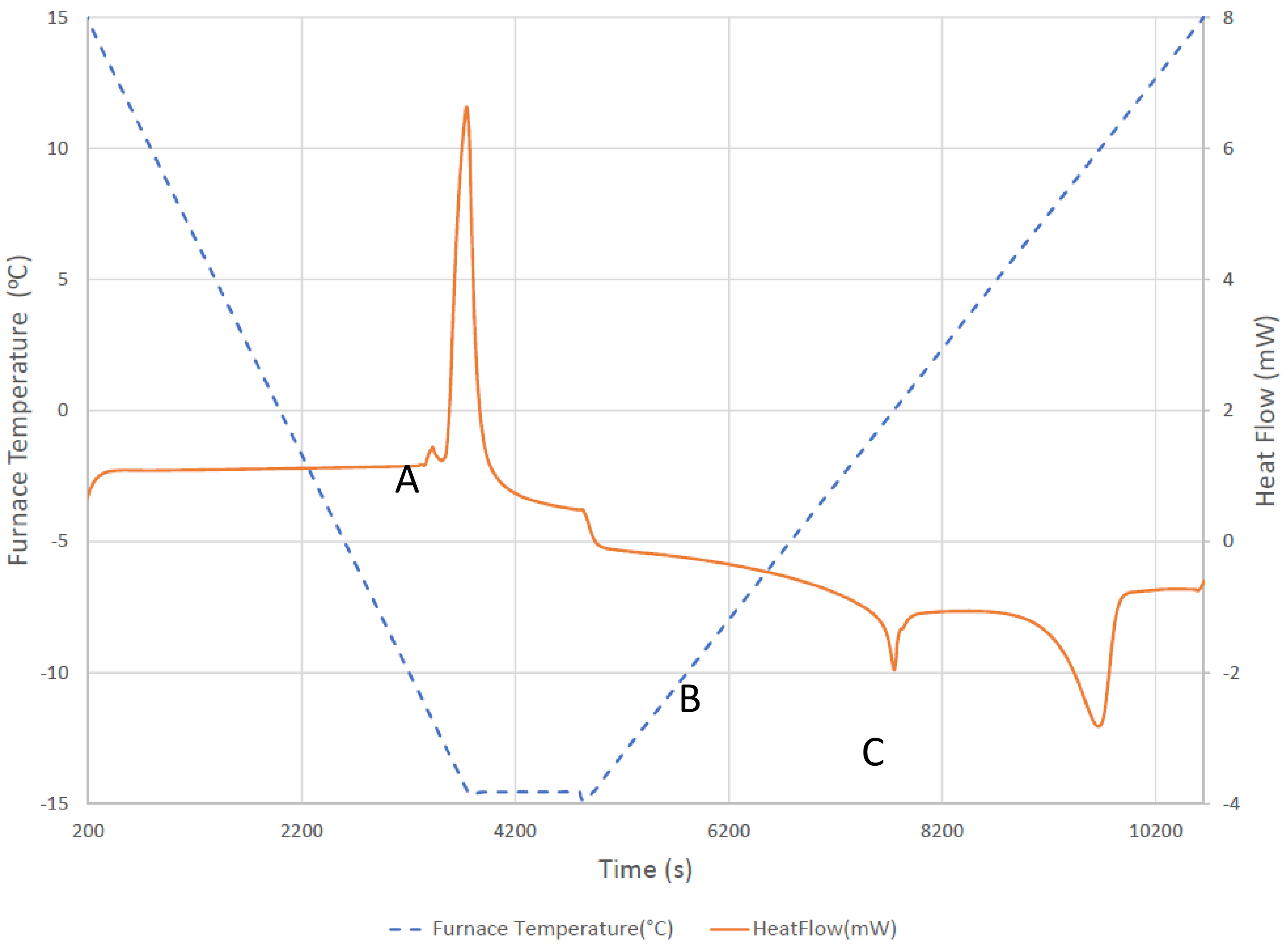
Micro Differential Scanning Calorimeter (DSC)



- **Phase equilibrium**
- **Heat of dissociation**
- **% Water conversion to hydrate**

DRG Daraboina Research Group

DSC Operating Procedure

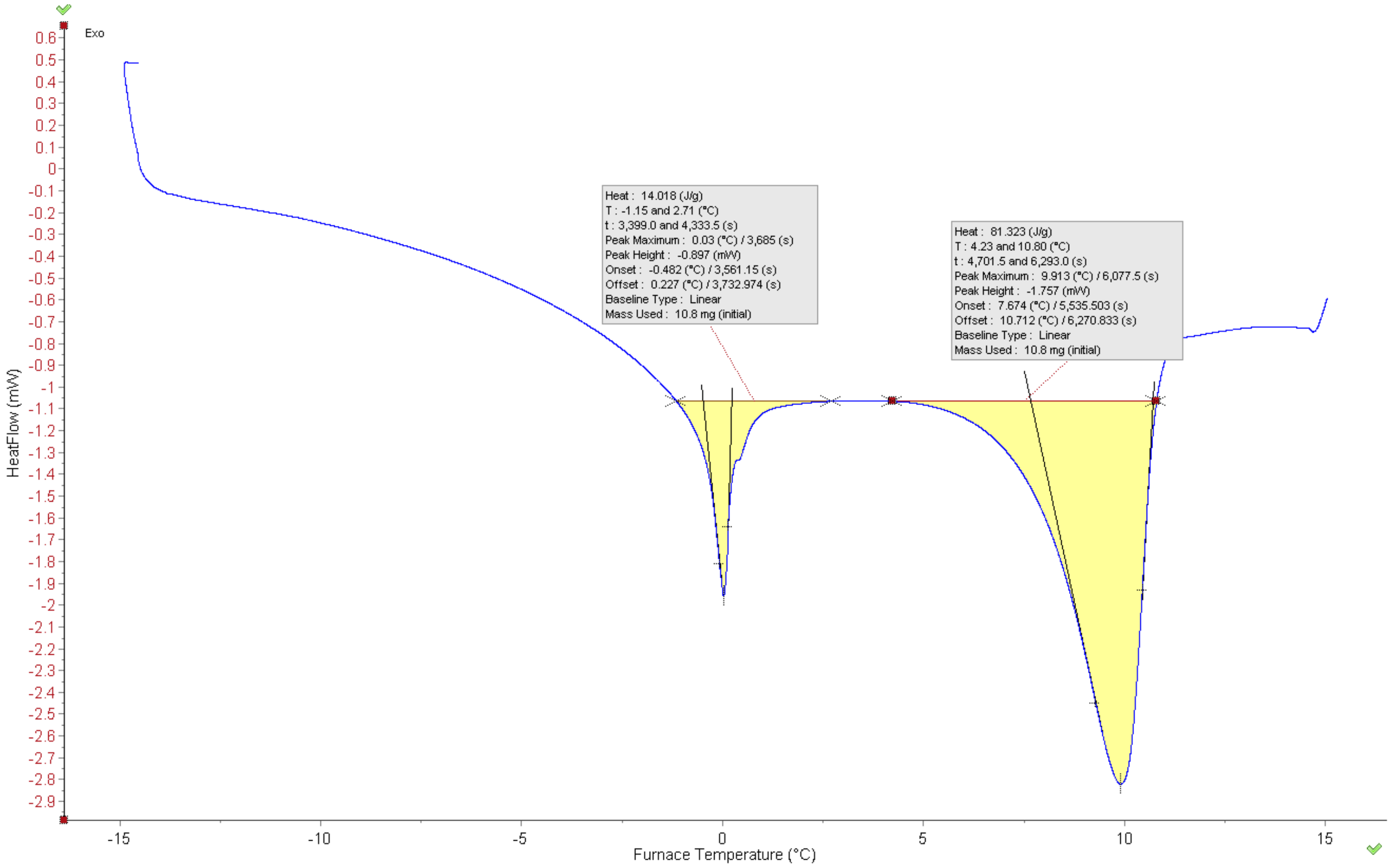


- **Cool from 15 ℃ to -15 ℃**
- **Hold temperature constant**
- **Heat back up to 15 ℃**

A. Formation Peak B. Ice Melting Peak C. Hydrate Melting Peak

DRG Daraboina Research Group

Water Conversion Calculation

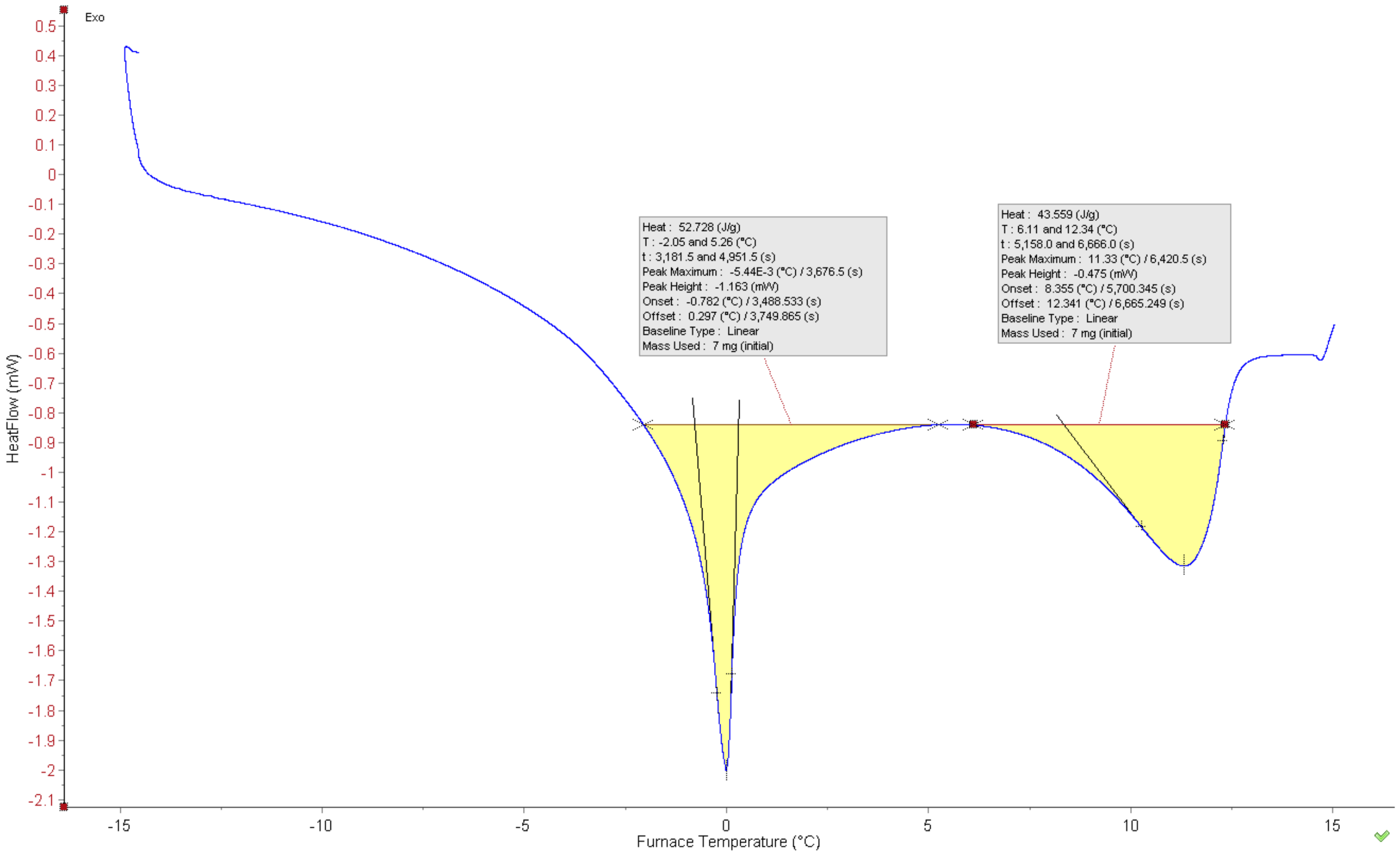


DSC curve for 20 wt% TBAB with out salts

- ΔH_{Water} = 333.78 J/g
- ΔH_{ICE} = 14.018 J/g
- $\Delta H_{Hydrate}$ = 81.323 J/g
- Sample W = 10.8mg
- ΔH_{ICE} = 0.1514 J/Sample
- W_{ICE} = 0.4536mg
- $W_{Hydrate}$ = 10.346mg
- Conversion = 95.8%

Daraboina Research Group

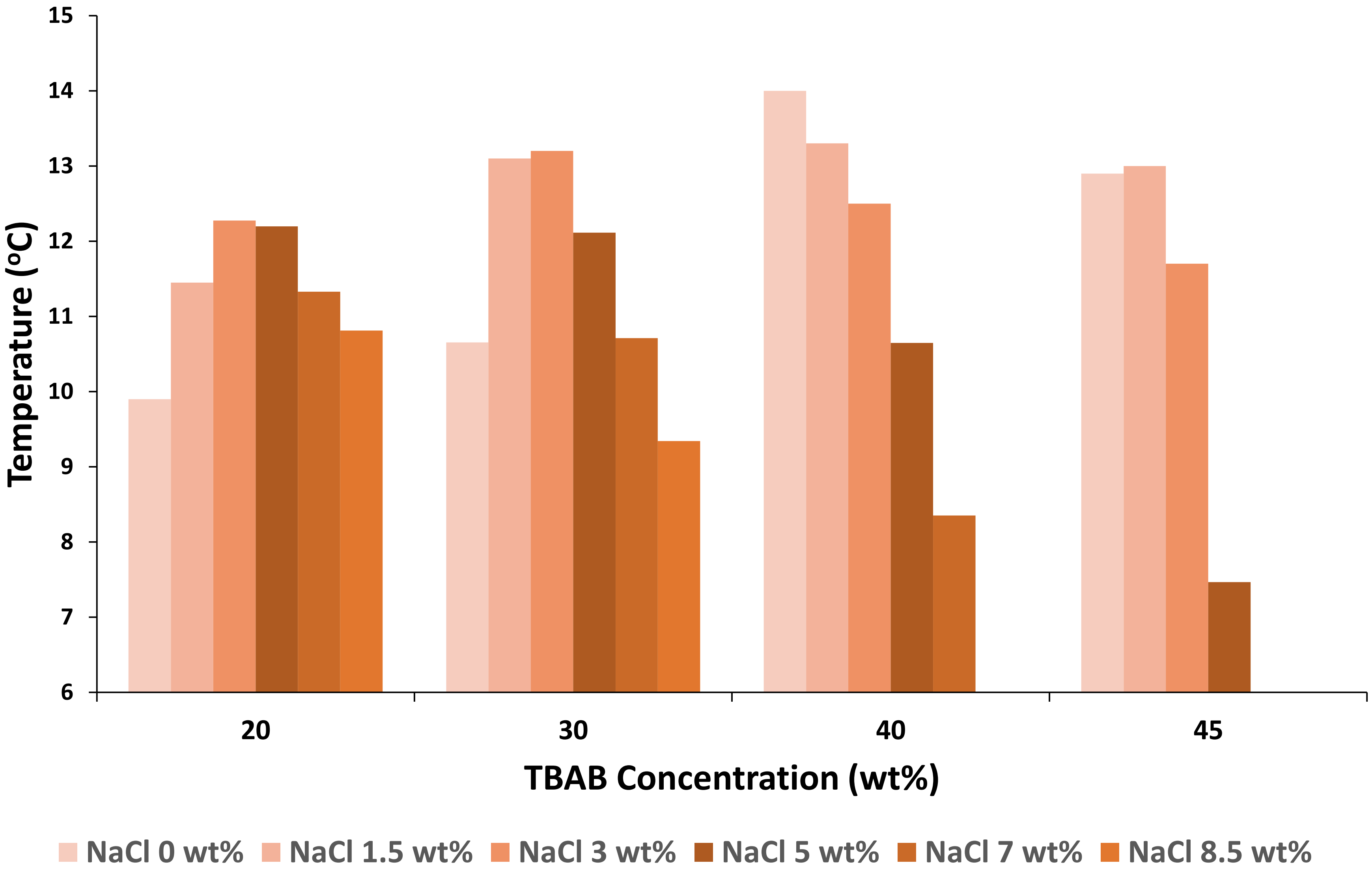
Water Conversion Calculation



DSC curve for 20 wt% TBAB with 7 wt% NaCl

- ΔH_{Water} = 333.78 J/g
- ΔH_{ICE} = 52.728 J/g
- $\Delta H_{Hydrate}$ = 43.559 J/g
- Sample W = 7mg
- ΔH_{ICE} = 0.369 J/Sample
- W_{ICE} = 1.1058mg
- $W_{Hydrate}$ = 5.894mg
- Conversion = 84.2%

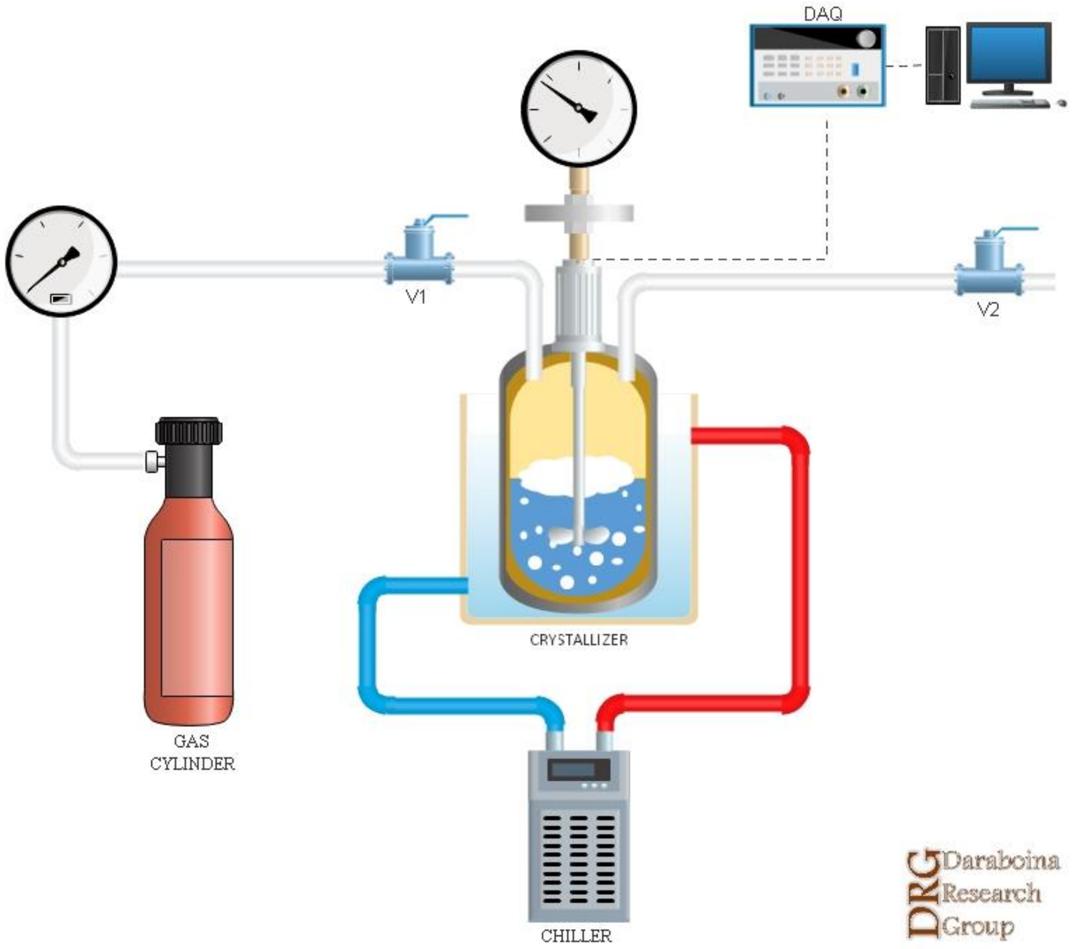
Phase Equilibrium curve



Daraboina Research Group

Small Scale Stirred Tank Reactor

- **Phase equilibrium**
- **Formation Kinetics**
  - **Induction time**
  - **Rate of hydrate formation**
  - **Total gas uptake**
- **Dissociation Kinetics**
- **% Water conversion to hydrate**



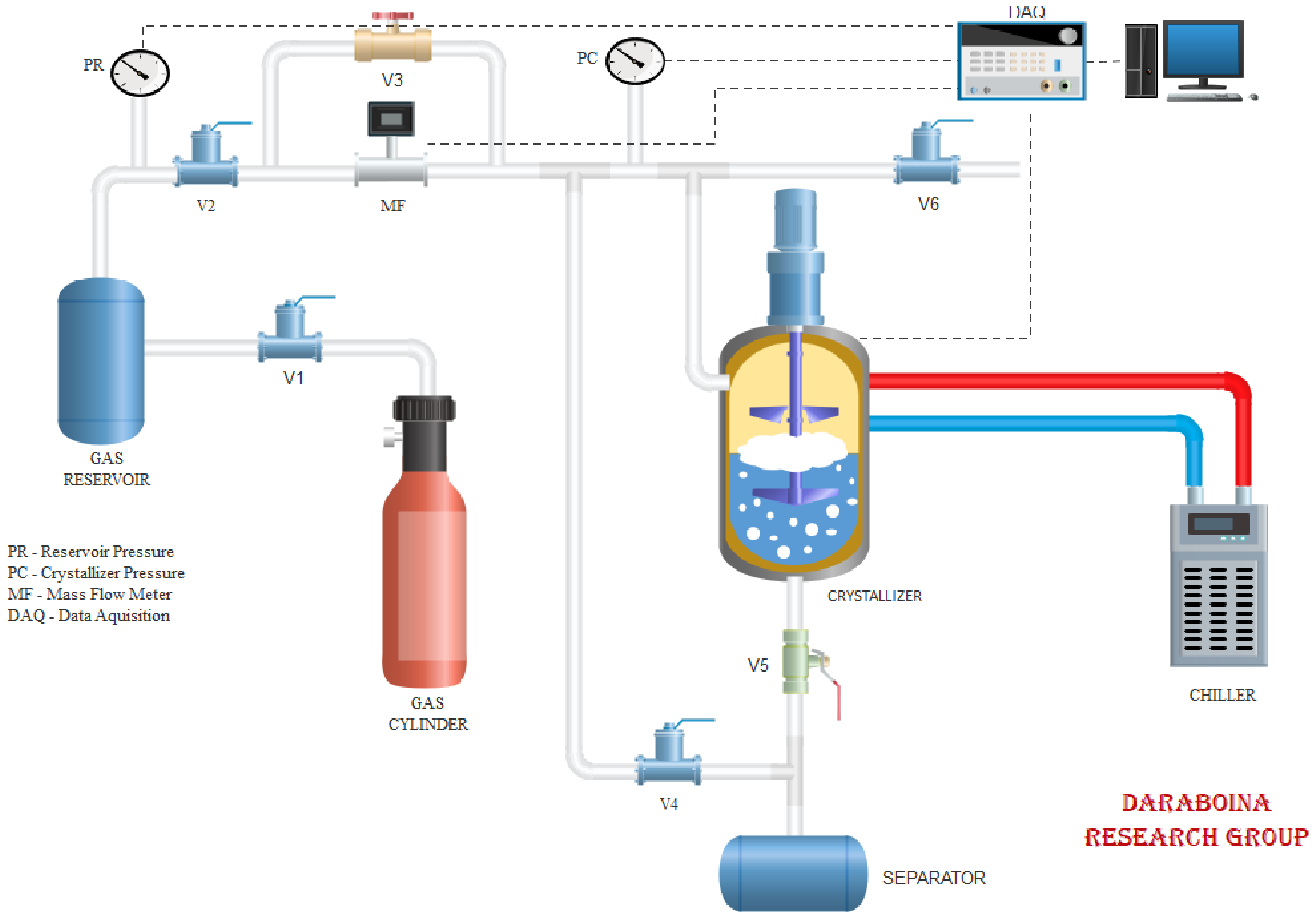
Daraboina Research Group

Isochoric Phase Equilibrium Measurement

Daraboina Research Group

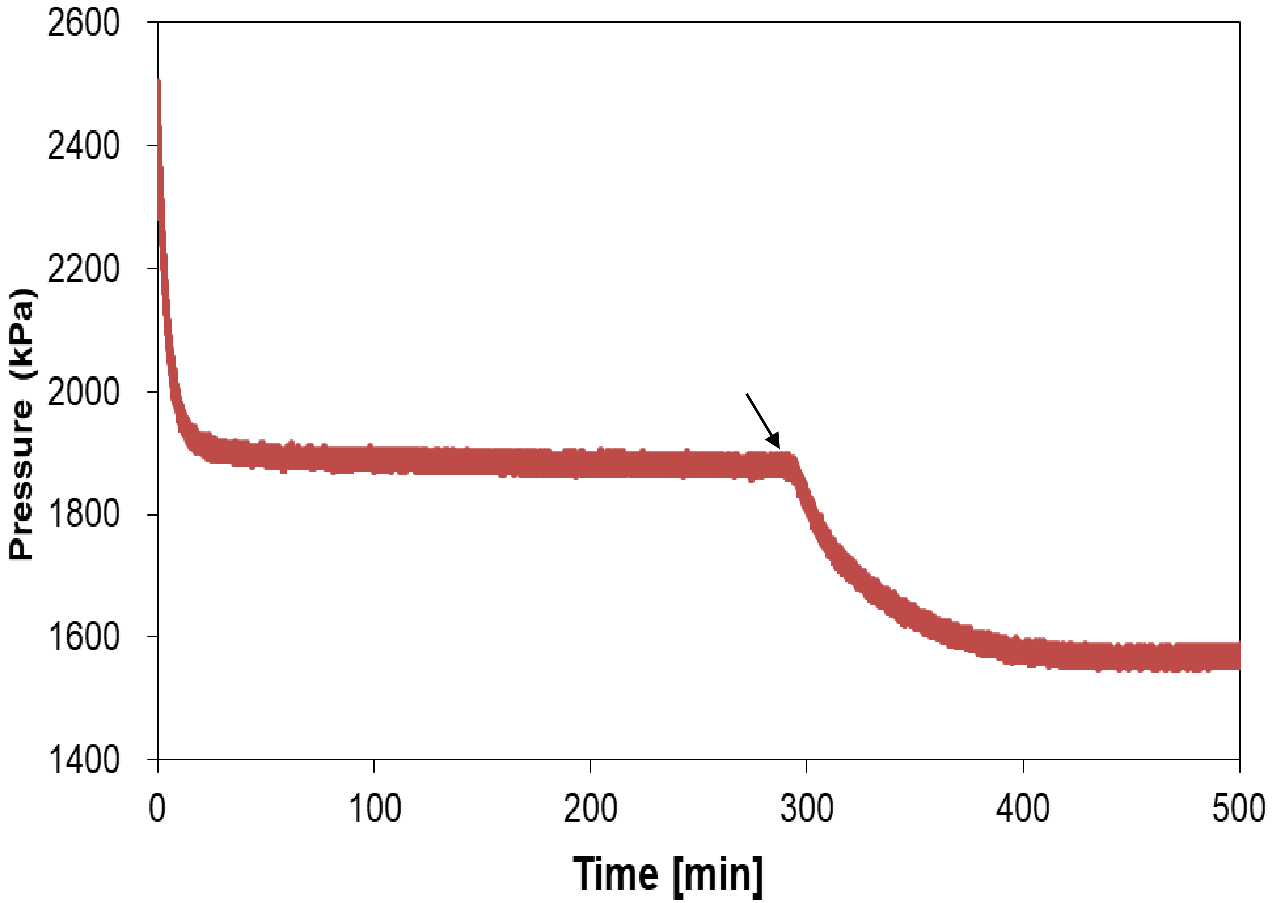
Prototype Reactor

- 4 L Reactor
- Pressure 1000 psi
- Temperature -10 °C to 40 °C

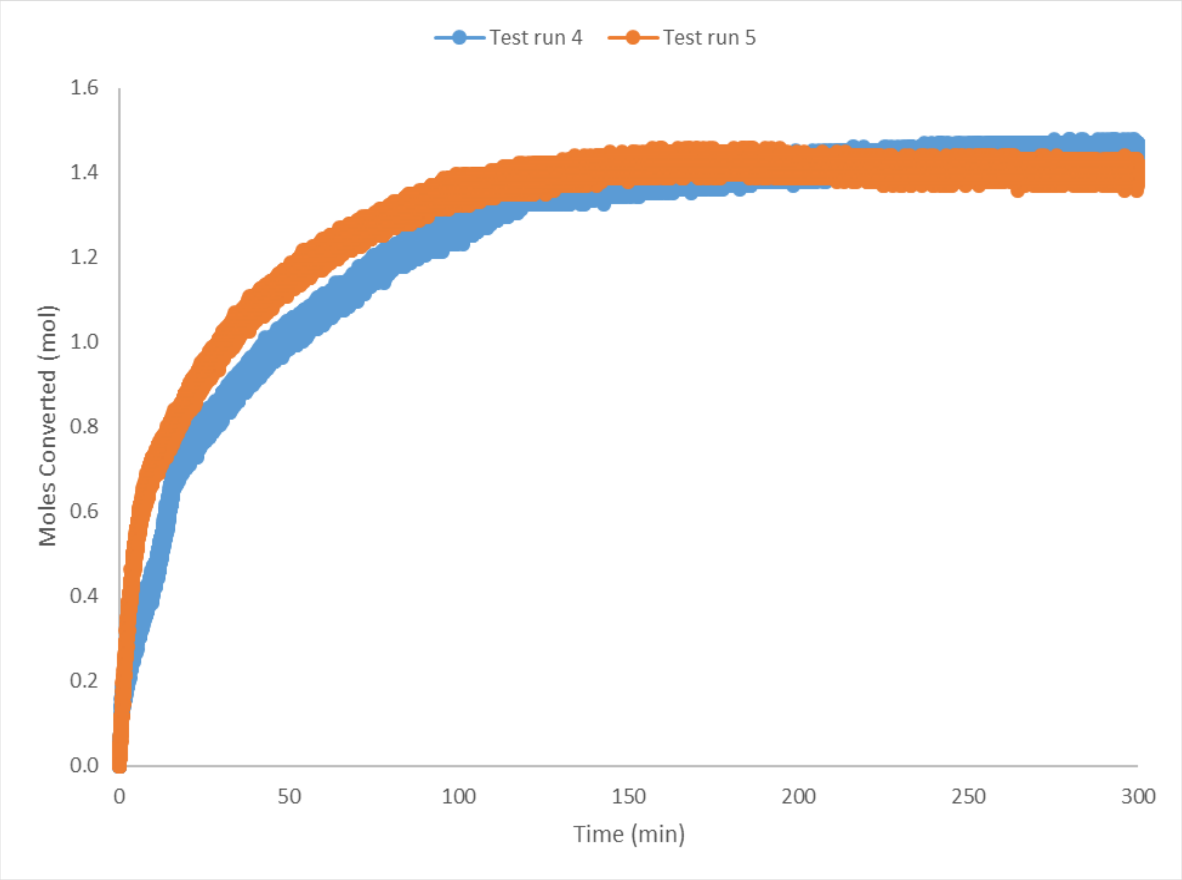


DRG Daraboina Research Group

Gas uptake measurement



Hydrate Growth curve



- Experiments with CO_2 at 360 PSI and 2.5 °C
- Repeatability

Summary

- Desalination via Clathrate Hydrate is a sustainable technology
- Need to identify a suitable hydrate former that can increase the operating temperature and enhances hydrate formation kinetics
  - Tetra-n-butyl ammonium bromide testing in progress

Moving forward

- To study kinetic water recovery experiments with different salts and different TBAB concentrations
- Salt rejection study at different concentrations of TBAB
- To optimize of operating conditions for maximum water recovery and salt rejection
- To evaluate OPEX and CAPEX

Process Simulation – Hysys

- ***Process simulation***
  - System integration and optimization of the process
  - Establish mass and energy balance
  - Determine water recoverable through system integration

- ***Economic analysis***
  - Sizing and costing of various process equipment
  - Analysis on operating costs incurred and determine cost of water

Acknowledgments

DRG Daraboina Research Group