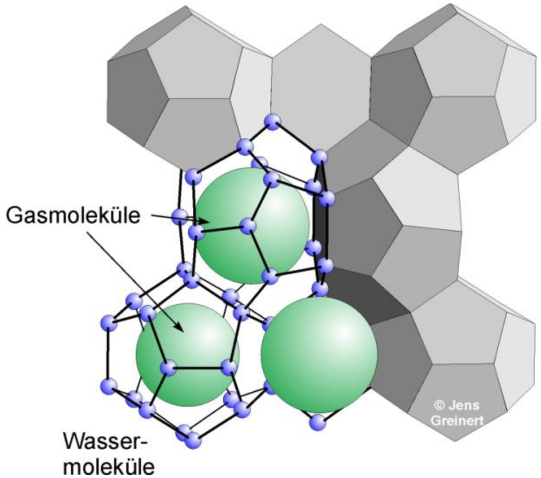
An Experimental Investigation Of Seawater Desalination By Gas Hydrate Formation

F. Knappitsch, G. Janicki, B. Egenolf-Jonkmanns, S. Bruzzano, G. Deerberg



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Fraunhofer UMSICHT

Outline

- Introduction
- Gas hydrate-based water desalination
- Materials and Methods
- Results
- Conclusion

Introduction

- Global increasing demand for fresh water in the future
- Scarcity of natural fresh water resources (only 3 % of the worlds water supply)
- Need for energy saving and affordable desalination technologies

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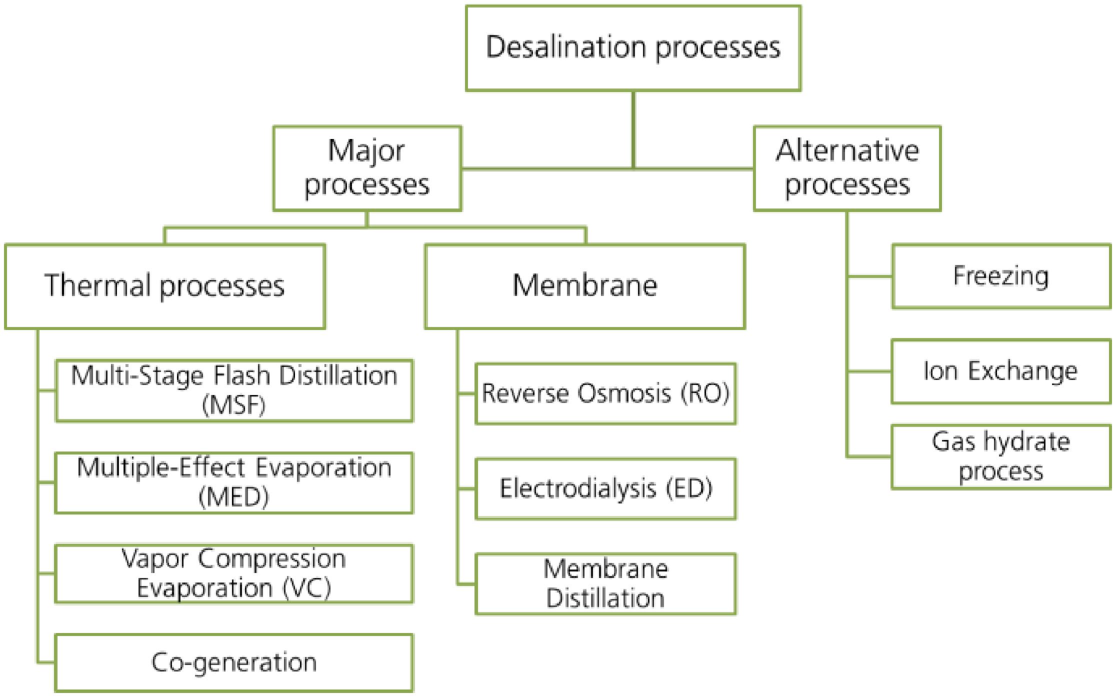

[Shatat and Riffat, 2012 (figure modified)]

Introduction

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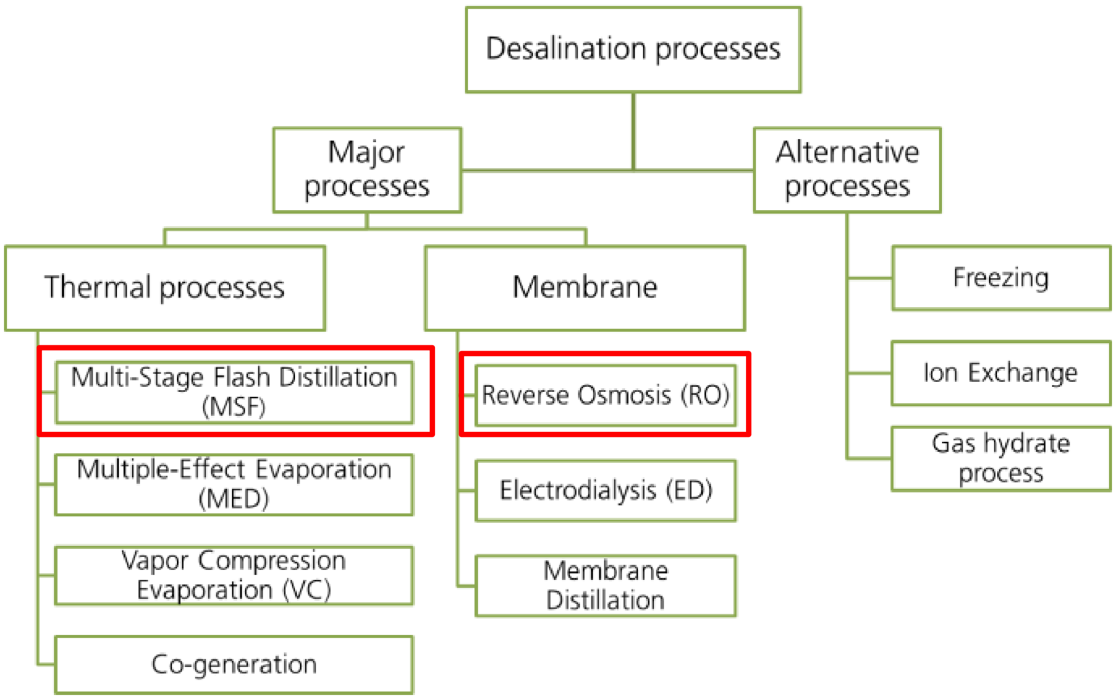
- Scarcity of natural fresh water resources (only 3 % of the worlds water supply)
- Need for energy saving and affordable desalination technologies



→ Conventional desalination technologies are energy- and cost-intensive

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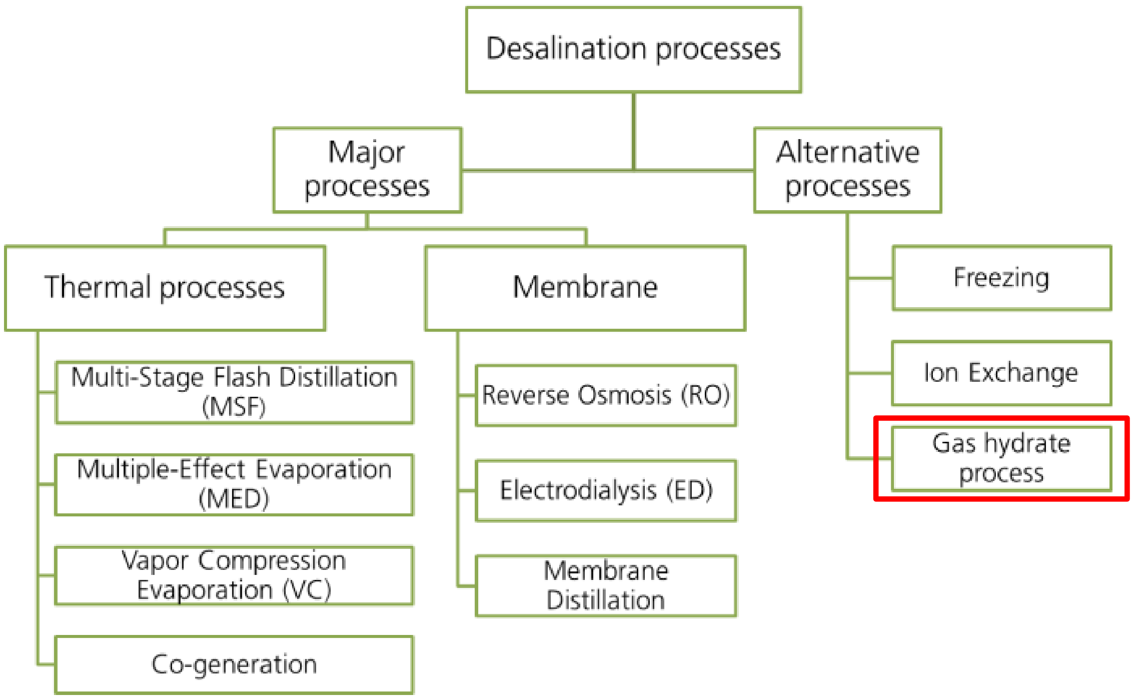
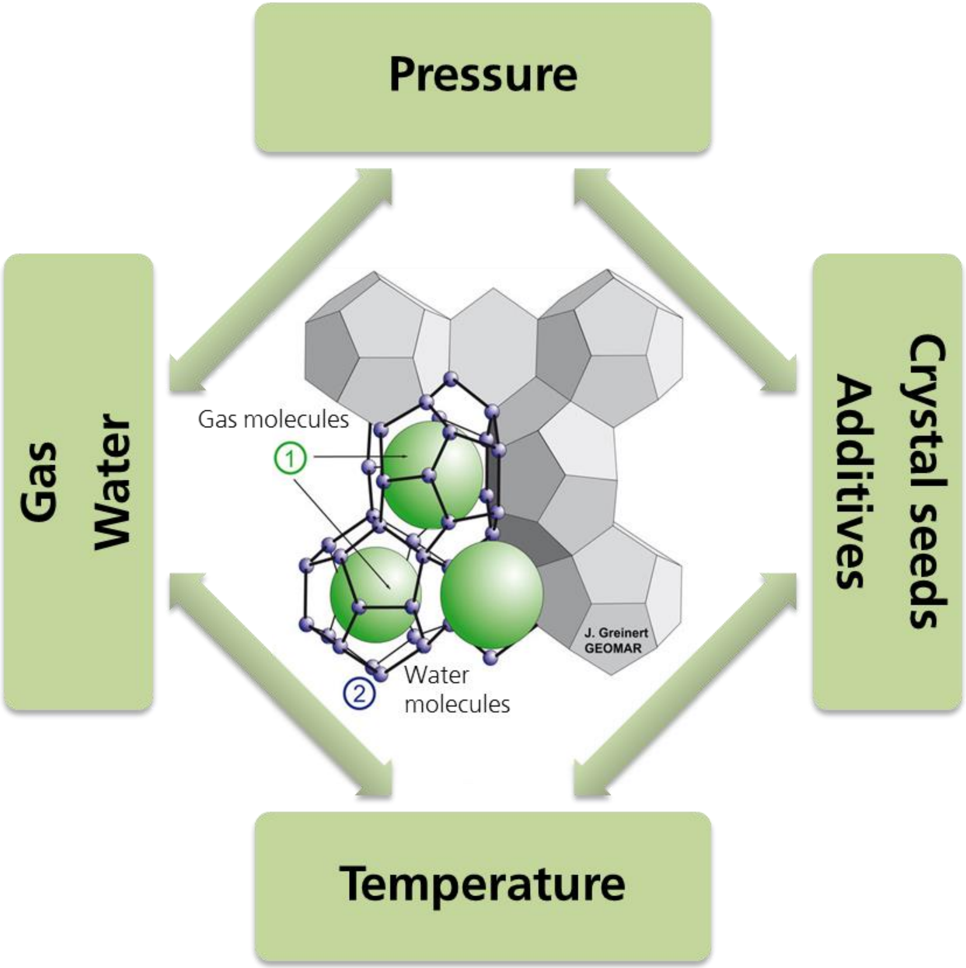


→ Hydrate-based technique has a high potential as desalination technology

What are gas hydrates?



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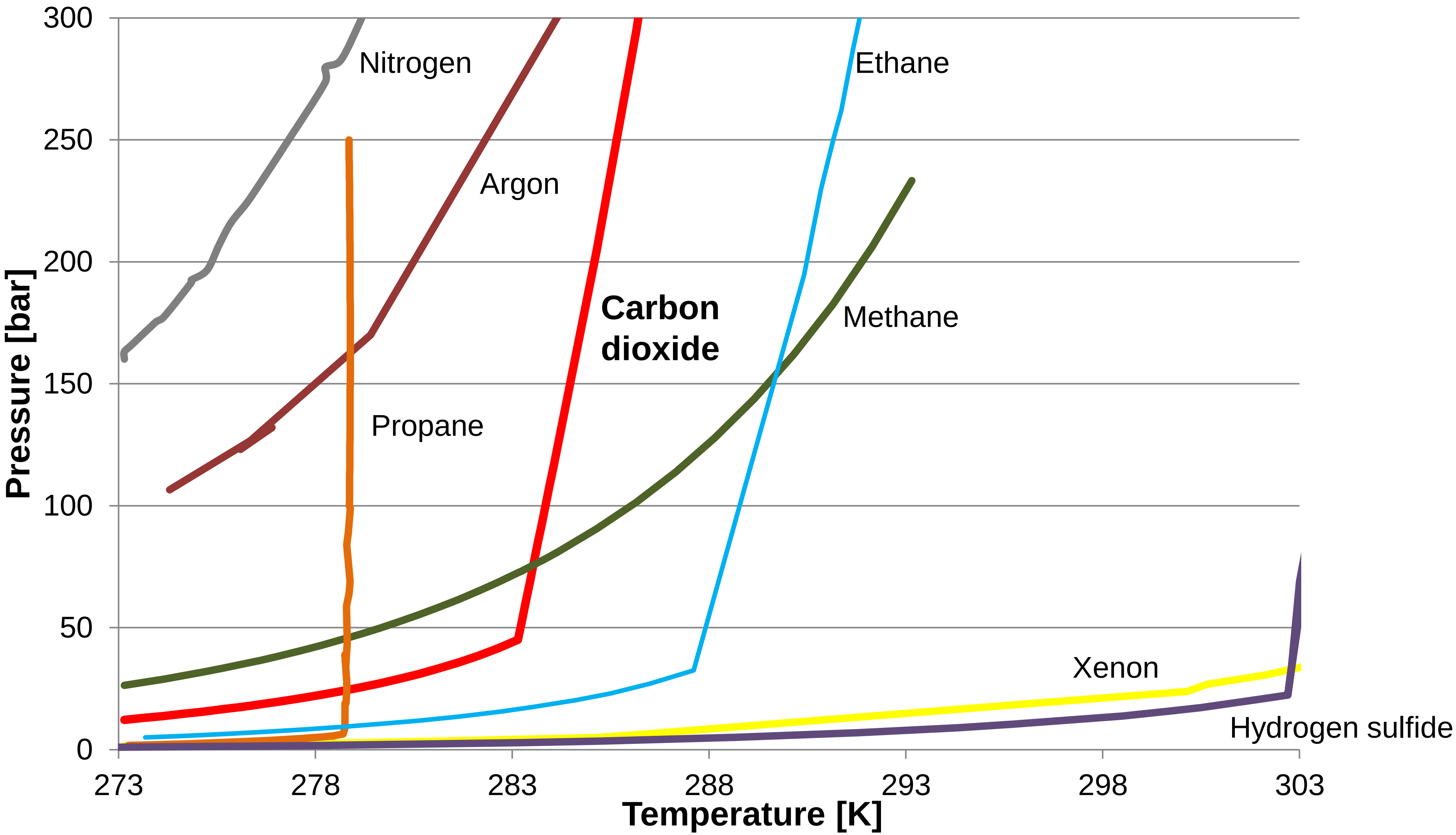
Stability of gas hydrates



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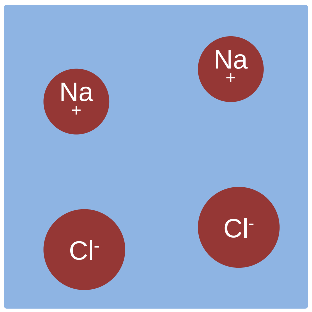
Gas hydrate-based water desalination



Sea water/
Brackish water

[Cha and Seol, 2013 (figure modified)]

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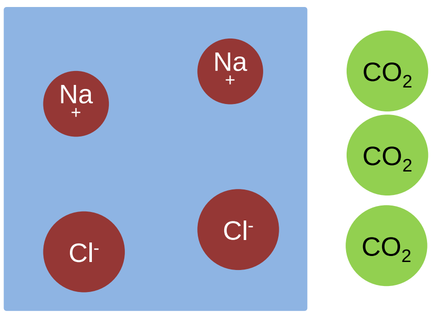

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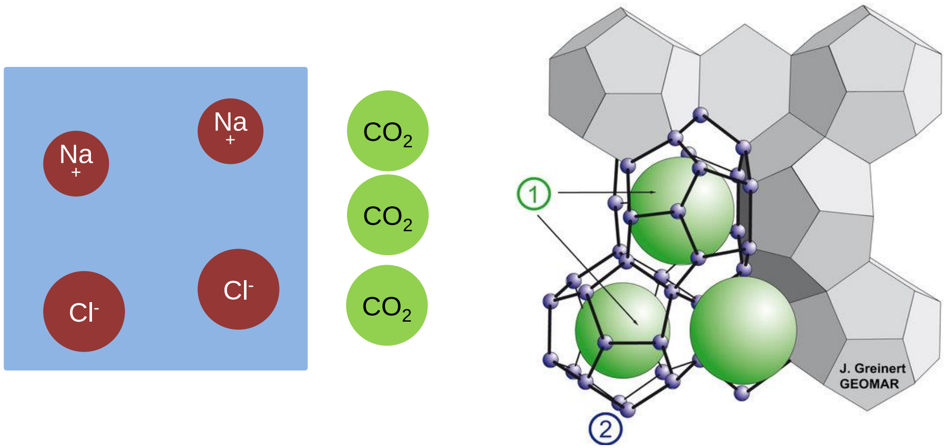


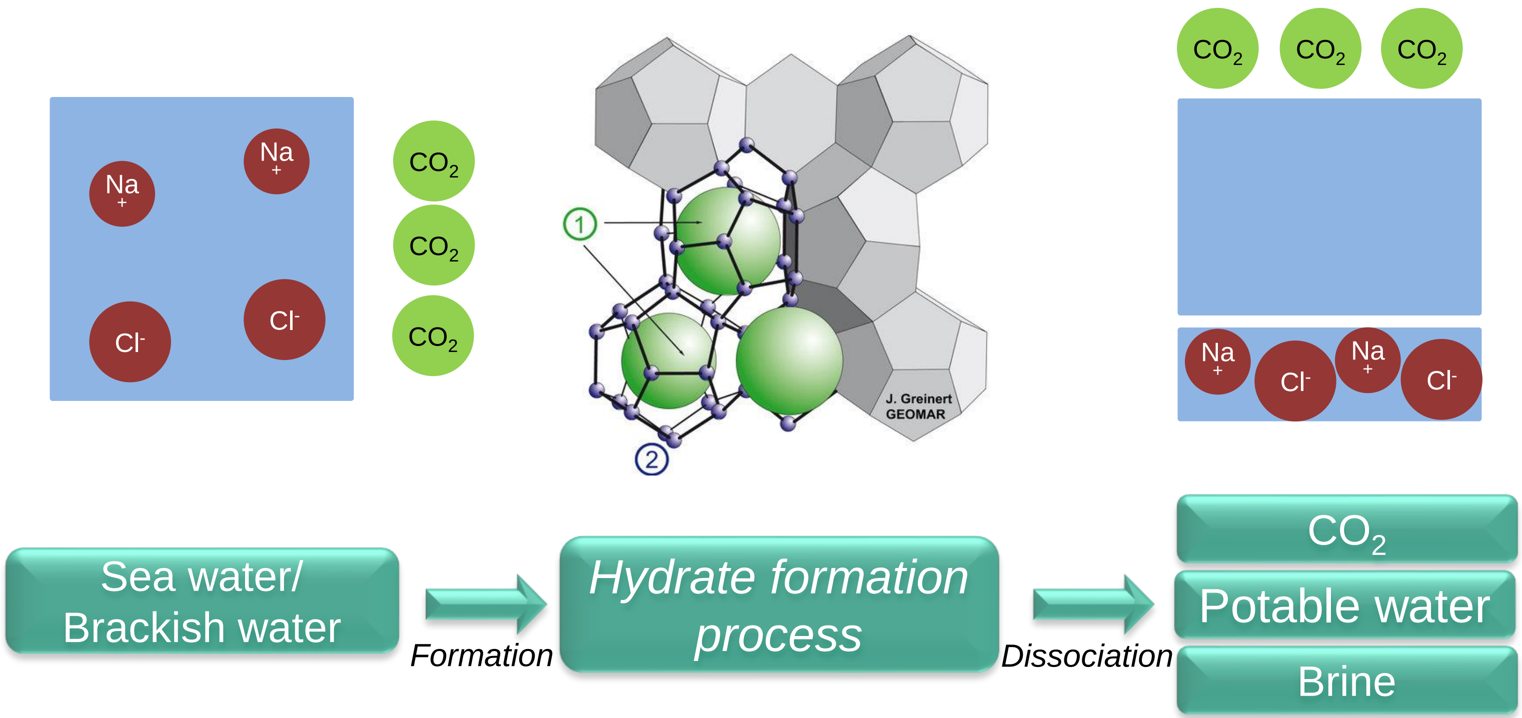
Sea water/
Brackish water

Formation

Hydrate formation process

[Cha and Seol, 2013 (figure modified)]

Gas hydrate-based water desalination



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Characteristics of different desalination technologies

Characteristics of different technologies	Gas hydrate process	Reverse Osmosis	Distillation
Preliminary water treatment	not required	required	not required
Pressure conditions	5 – 50 bar	~ 60 bar	p_a
Temperature conditions	5 – 20 °C	T_a	90 - 120 °C
Heat of phase change	507 kJ/kg_{H2O}	No phase change	2256,7 kJ/kg
Energy consumption [$kJ/kg_{fresh\ water}$]	< 100 (Depends on hydrate former, number of stages etc.)	< 100	> 300
Salt content in water produced [g/L]	0 (in theoretical)	< 1	0
Operating and material costs	medium (moderate temperature, insensitivity to biological fouling, scaling and corrosion problems)	high (Fouling and scaling problems, short membrane lifetime)	high (corrosion problems)

[McCormack, 1995; van der Bruggen, 2002; Fournaison, 2004; Miller, 2013; Roger, 1994; Shatat, 2012]

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Materials and Methods: Experimental setup

High pressure tank reactor (V = 540 mL)

Operating conditions:

- p_{max} = 200 bar
- -30 ≤ T ≤ 300 °C
- N_{max} ≤ 650 rpm

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Materials and Methods: Experimental setup

High pressure tank reactor (V = 540 mL)

Operating conditions:

- p_{max} = 200 bar
- -30 ≤ T ≤ 300 °C
- N_{max} ≤ 650 rpm

- Target parameters:
  - **Salt removal efficiency** for
    - a batch (single- and two-stage) process
    - different post-treatment methods (washing, melting, vacuum filtration)
  - Impact of **process time** (begin nucleation – end of exp.) and **water conversion**

Materials and Methods: Experimental procedure

Batch process (single-stage)

1. CO_2 hydrate formation
   - Synthetic seawater (150 mL; salinity of 3.5 wt.%)
   - Process conditions: 50 bar, 1 °C, N = 500 rpm
2. Phase separation of hydrates and brine
3. Hydrate dissociation
   - Measuring of electrical conductivity
   - Calculation of separation efficiency

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   - Calculation of separation efficiency

$$\eta\ [\%] = \frac{c_i - c_h}{c_i} * 100$$

Materials and Methods: Experimental procedure

Batch process (two-stage)

1. CO_2 hydrate formation
   - Synthetic seawater (150 mL; salinity of 3,5 wt.%)
   - Process conditions: 50 bar, 1 °C, N = 500 rpm
2. Phase separation of hydrates and brine
3. Hydrate dissociation
   - Measuring of electrical conductivity
   - Calculation of separation efficiency
4. Reuse of dissociated hydrate phase (Second hydrate formation)

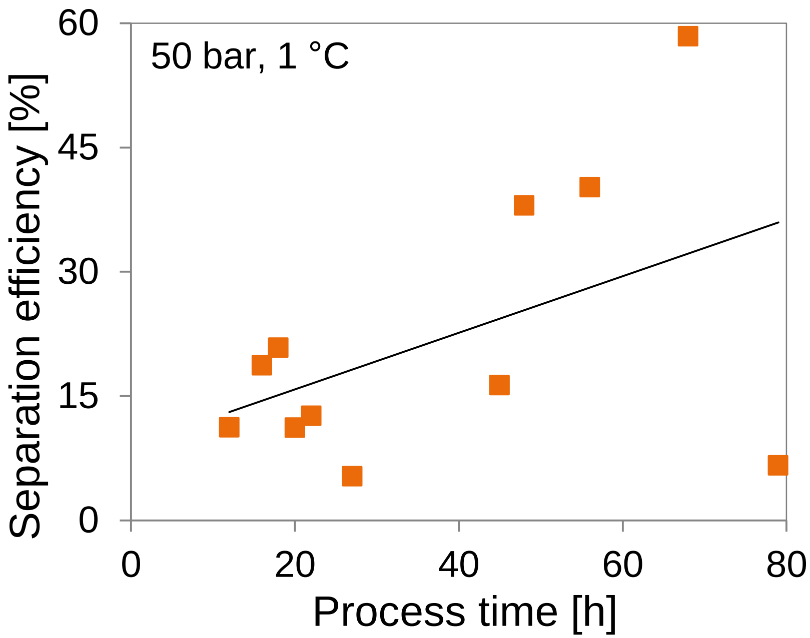
Materials and Methods: Experimental procedure

Batch process+Post-treatment

1. CO_2 hydrate formation
   - Synthetic seawater (150 mL; salinity of 3.5 wt.%)
   - Process conditions: 50 bar, 1 °C, N = 500 rpm
2. Phase separation of hydrates and brine
3. Post-treatment of hydrate phase (Washing, melting (for 15 min), vacuum filtration)
4. Hydrate dissociation
   - Measuring of electrical conductivity
   - Calculation of separation efficiency

Results: Batch process (single-stage)

Process time



→ Separation efficiency between 5.3 and 58.4 % (22 % on average)

→ Long process time promotes the purity of the hydrate phase

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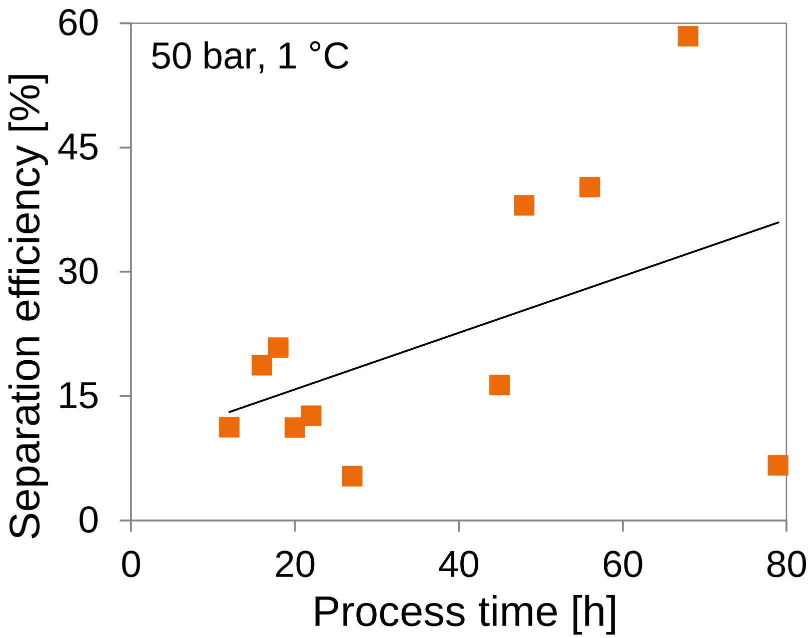
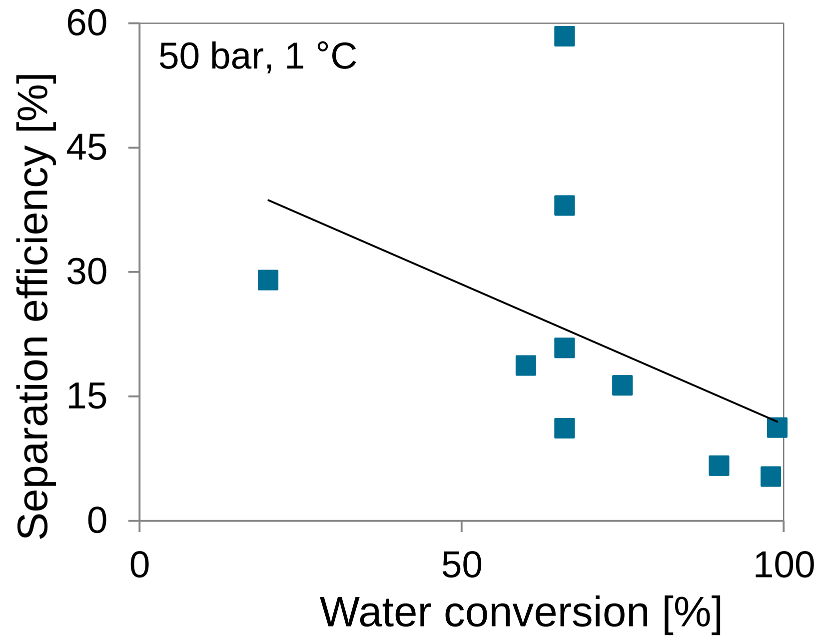
Results: Batch process (single-stage)

Process time



Water conversion

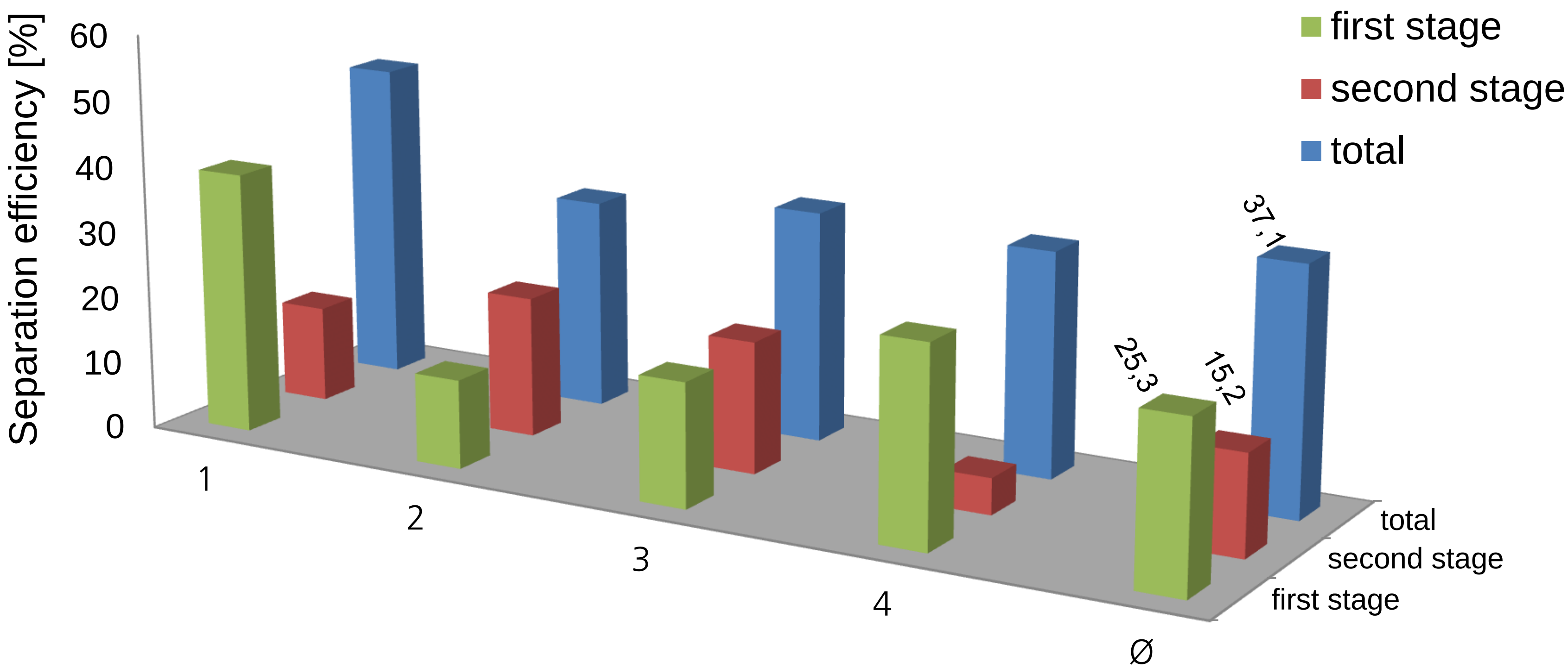


→ Separation efficiency between 5.3 and 58.4 % (22 % on average)

→ Long process time promotes the purity of the hydrate phase

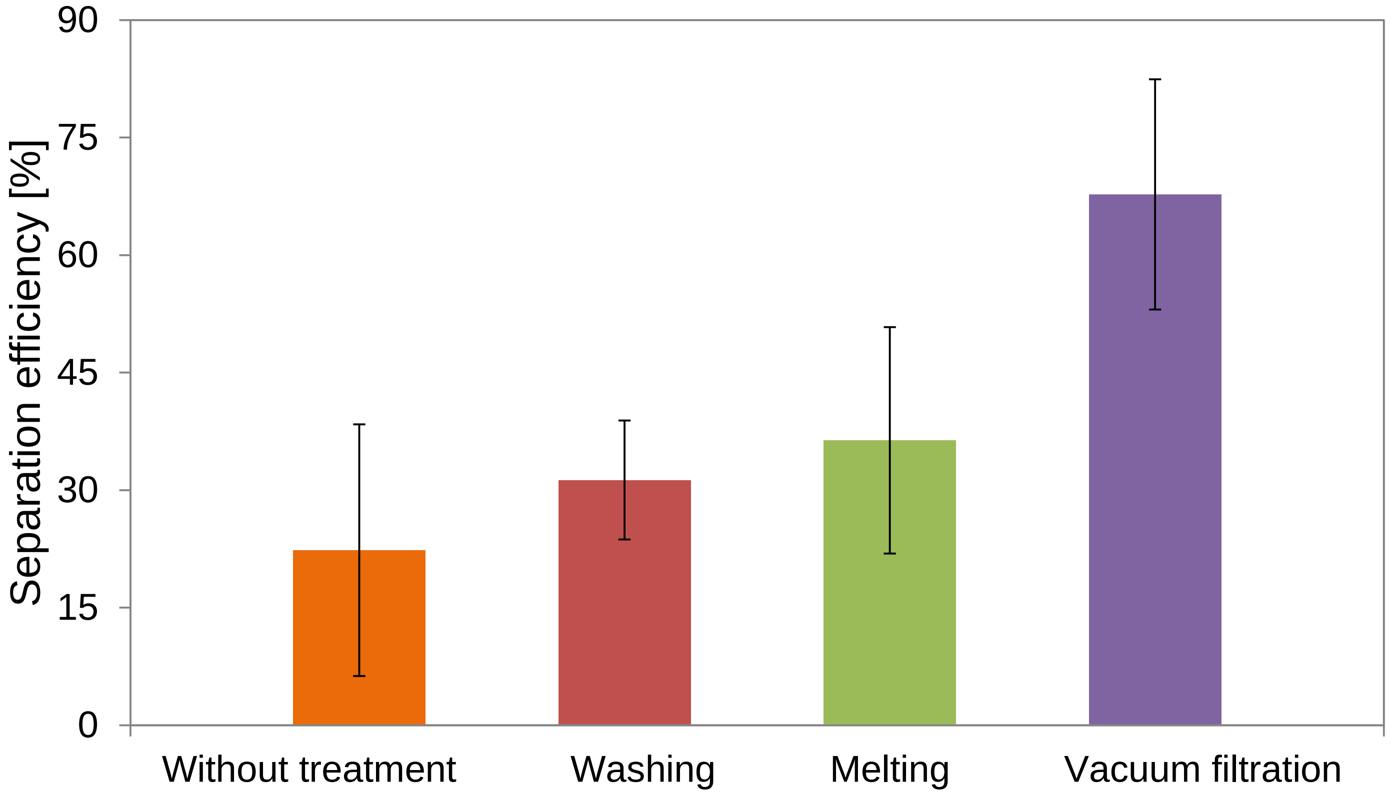
→ Increase in water conversion leads to lower separation efficiencies

Results: Batch process (two-stage)



→ Separation efficiency could be increased by around 15 % on average

Results: Post-treatment methods



→ Vacuum filtration is the most effective of the three methods (increase from 22 % up to nearly 68 % on average)

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Results: Separation efficiency in different hydrate section

- Problem: Significant amount of remaining impurities in hydrate bulk
  - adsorption of impurities on hydrate surface
  - porosity of hydrate bulk
  - dendritic nature of hydrate particles and high amount of interstitial water

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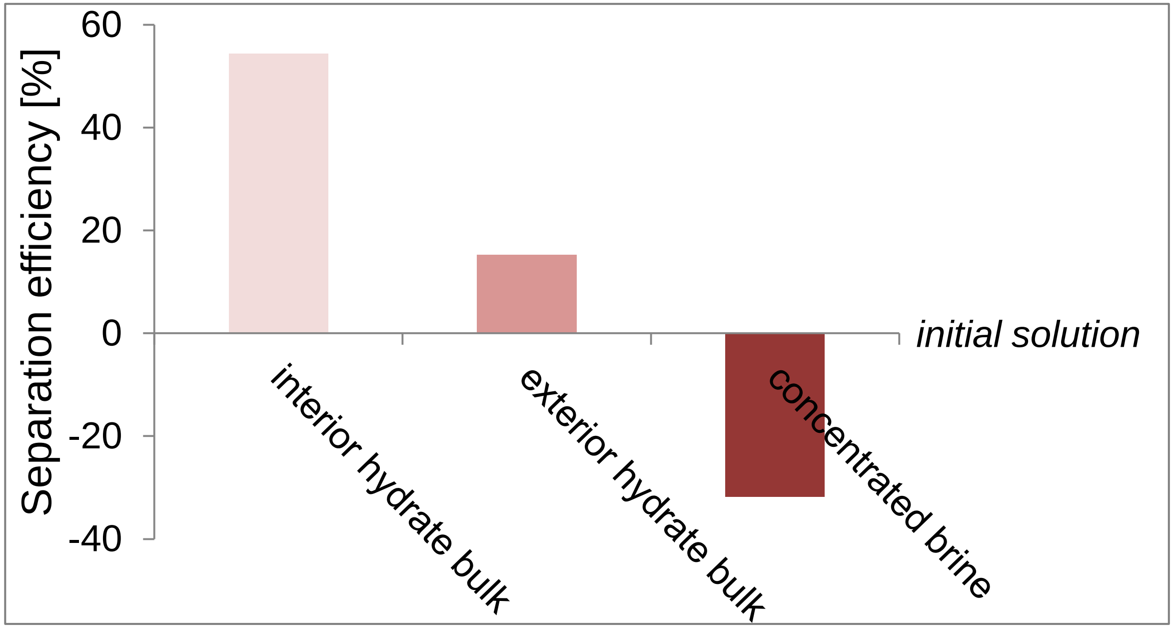
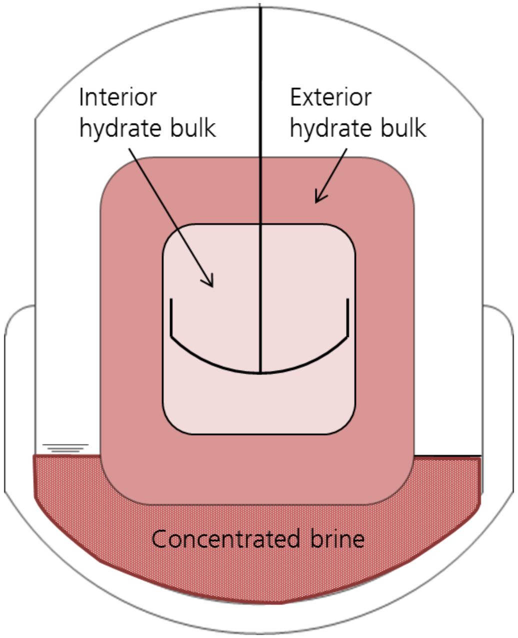
- Problem: Significant amount of remaining impurities in hydrate bulk
  - adsorption of impurities on hydrate surface
  - porosity of hydrate bulk
  - dendritic nature of hydrate particles and high amount of interstitial water
- Detection of the position of impurities in hydrate bulk





Results: Hydrate formation from blackcurrant juice

- Hydrate formation from blackcurrant juice
- Visual observation of the position of remaining impurities in hydrate phase

→ Pigment concentration varies in different hydrate sections

→ Validation of the theory

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Conclusion

- Separation efficiencies between 5 % and 70 % were achieved

  → Stage-wise process and post-treatment methods enhance the salt removal

- Purity of hydrate phase depends on different factors (water conversion, process time,..)

- Need for further research to understand the separation mechanism

  → Change of morphological characteristics (dendritic growth, interstitial water) and physical-chemical properties

  → Scale-up and technical implementation (e. g. phase separation, apparatus design for continuous operating mode)

Thank you for your attention!

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