ETH zürich

Ternary phase diagrams and experimental investigation of the particle formation kinetics for the CO_2-NH_3-H_2O system

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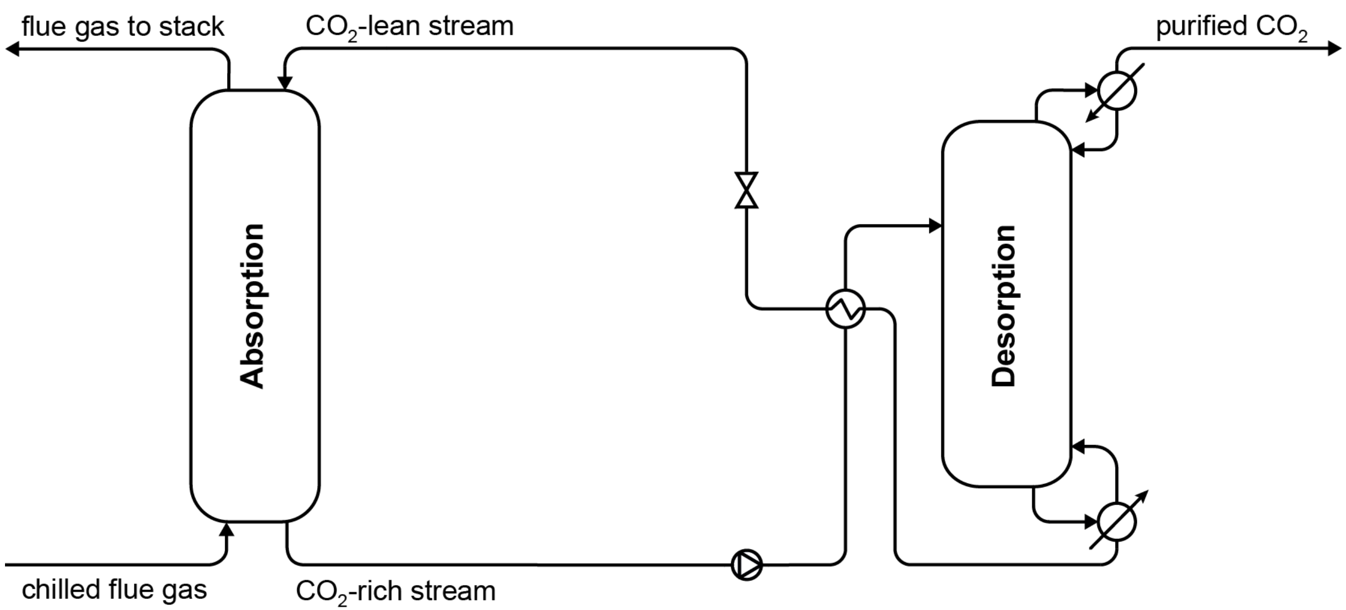
Motivation: The Chilled Ammonia Process (CAP)



- **Aqueous ammonia** as solvent ⇨
  - ✓ globally available, low cost
  - ✓ no toxic degradation products
  - ✓ highly competitive energy penalty

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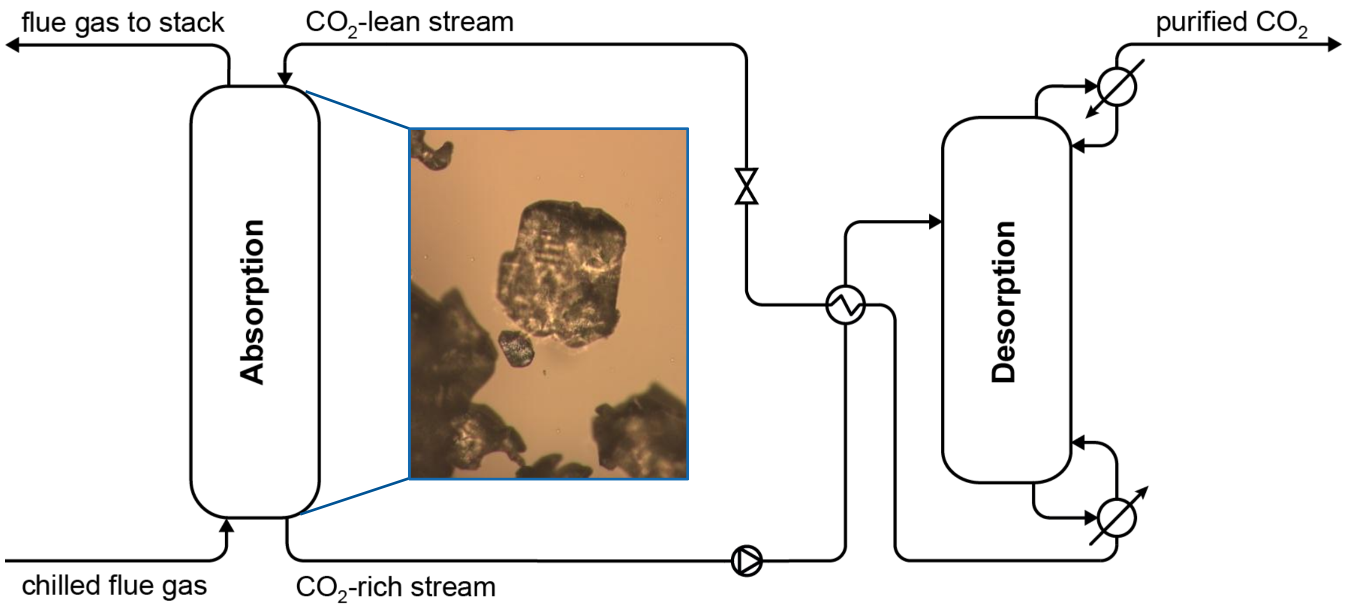

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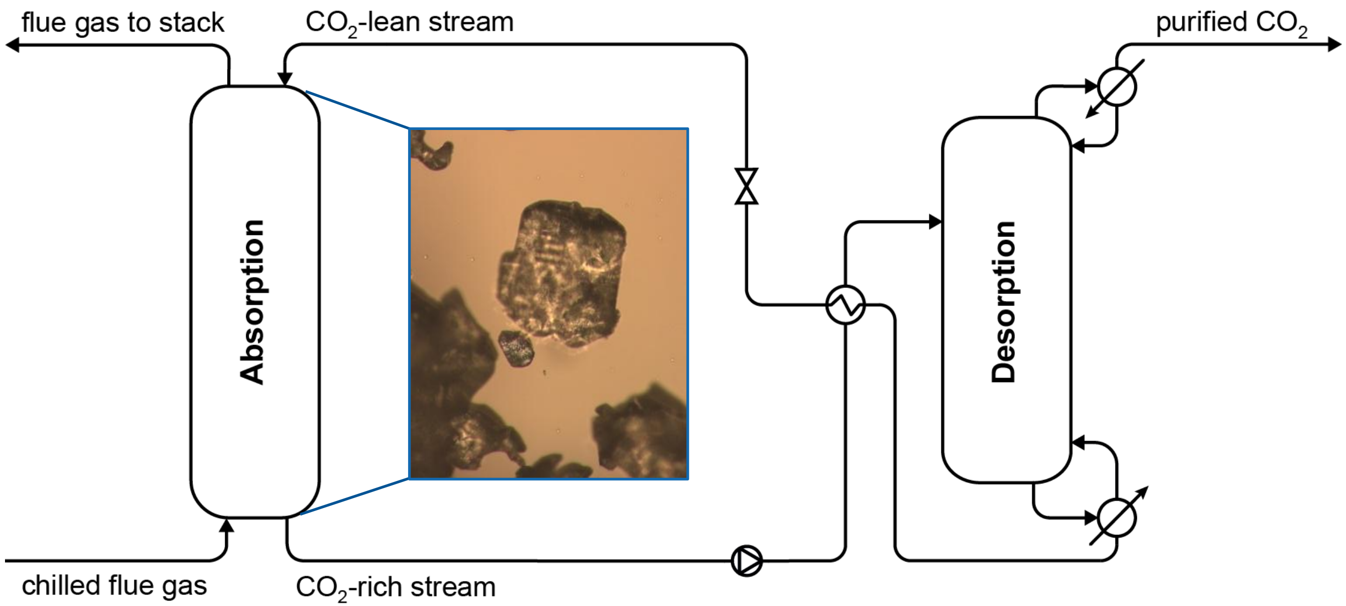
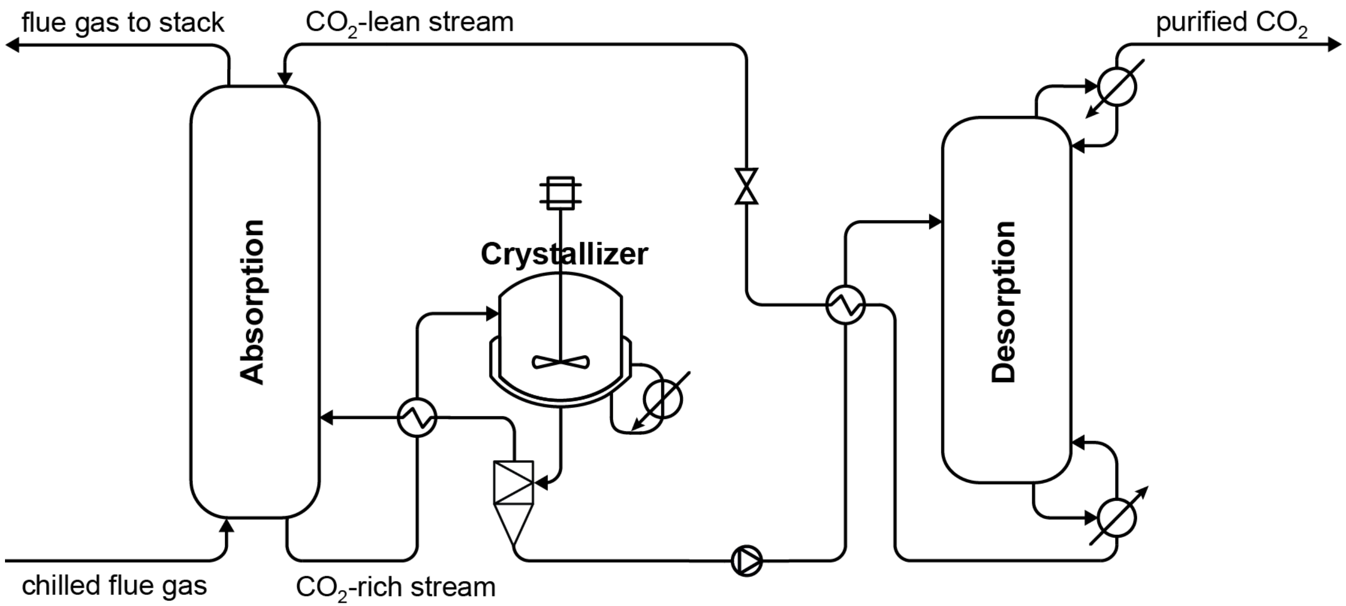
Strategic project objectives



Study the formation of solids in the CO_2-NH_3-H_2O system in order to

a) enable high CO_2 concentrations while **avoiding solid formation** in the absorber in the current CAP

Strategic project objectives



Study the formation of solids in the CO_2-NH_3-H_2O system in order to

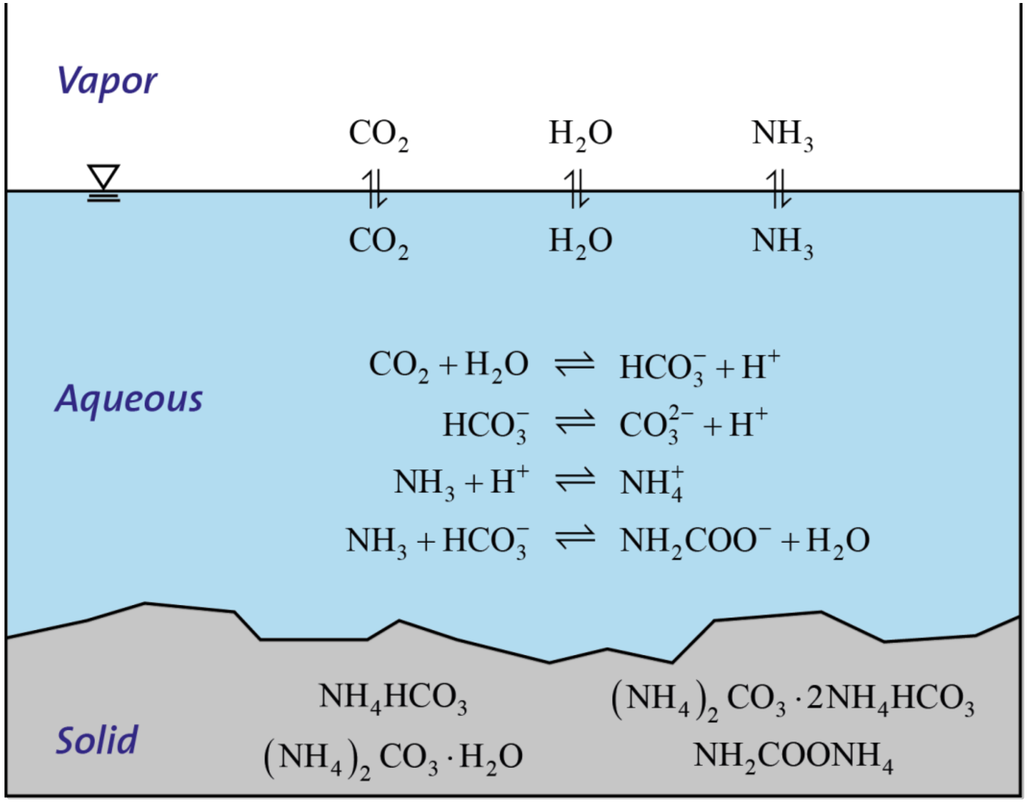
a) enable high CO_2 concentrations while **avoiding solid formation** in the absorber in the current CAP

b) **integrate solid formation** into a next generation CAP

Outline

- Thermodynamics
  - The system CO_2-NH_3-H_2O
  - Ternary phase diagrams
- Experimental
  - Methodology
  - Identification of solids by Raman
- Process simulations
  - Process model
  - Comparison of standard CAP & crystallizer-CAP

Thermodynamics of the CO_2-NH_3-H_2O system



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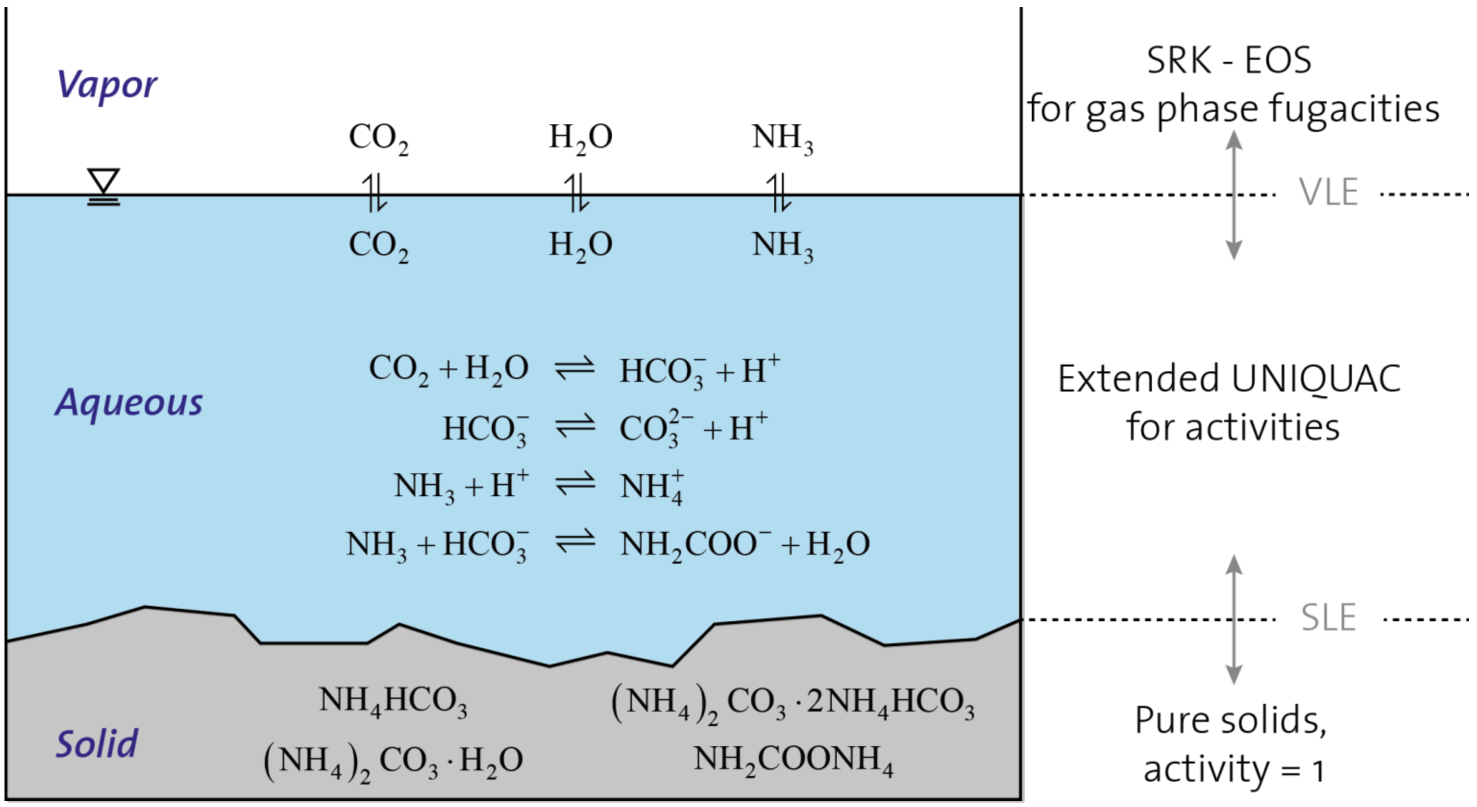
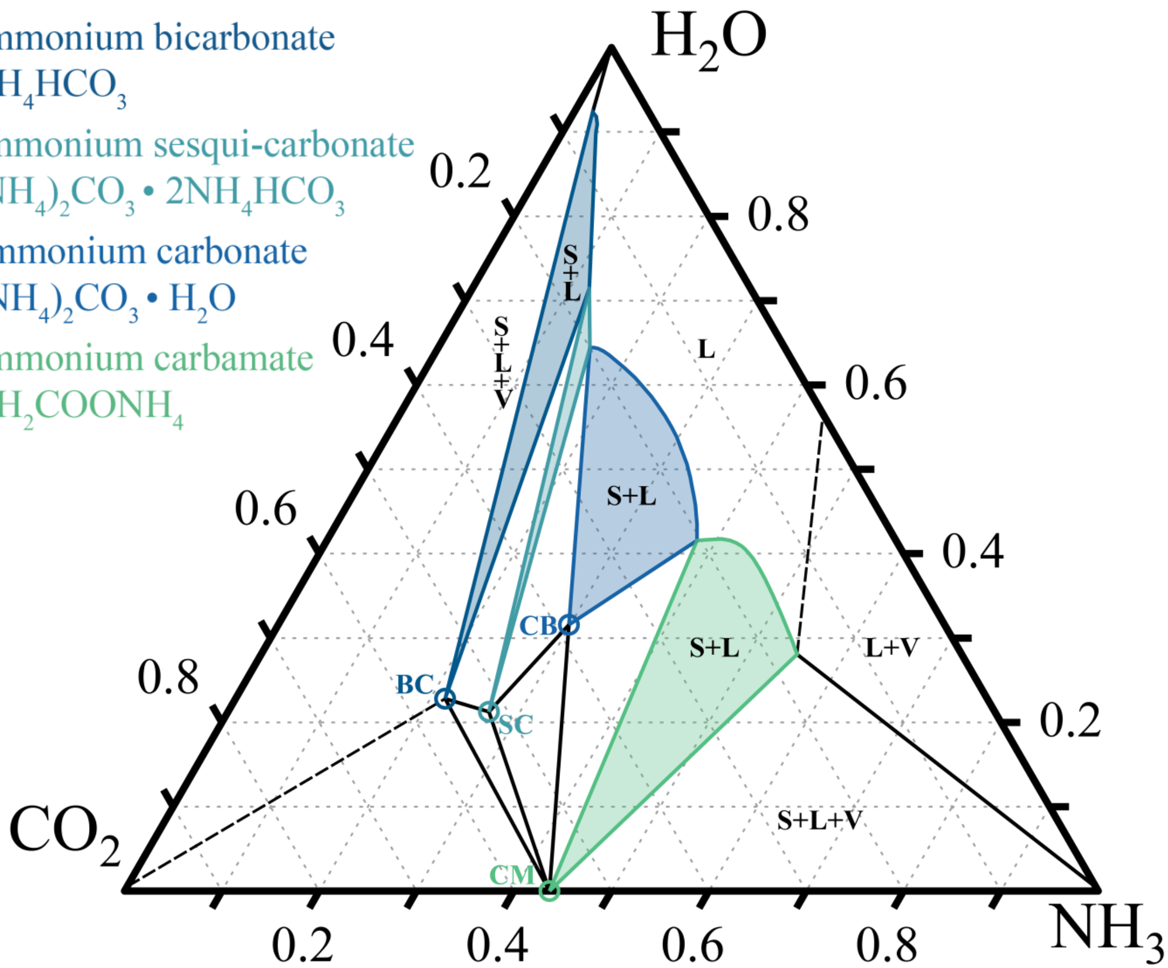


Thermodynamic model: Darde et al., *Ind Eng Chem Res* 49 (2010) 12663-74
Solid properties: Jänecke, *Z Elektrochem* 35 (1929) 9:716-28

Ternary phase diagram

BC	ammonium bicarbonate NH_4HCO_3
SC	ammonium sesqui-carbonate $(NH_4)_2CO_3 \cdot 2NH_4HCO_3$
CB	ammonium carbonate $(NH_4)_2CO_3 \cdot H_2O$
CM	ammonium carbamate NH_2COONH_4



10°C, 1 bar

Ternary phase diagram – Stoichiometry

BC ammonium bicarbonate
NH_4HCO_3

SC ammonium sesqui-carbonate
$(NH_4)_2CO_3 \cdot 2NH_4HCO_3$

CB ammonium carbonate
$(NH_4)_2CO_3 \cdot H_2O$

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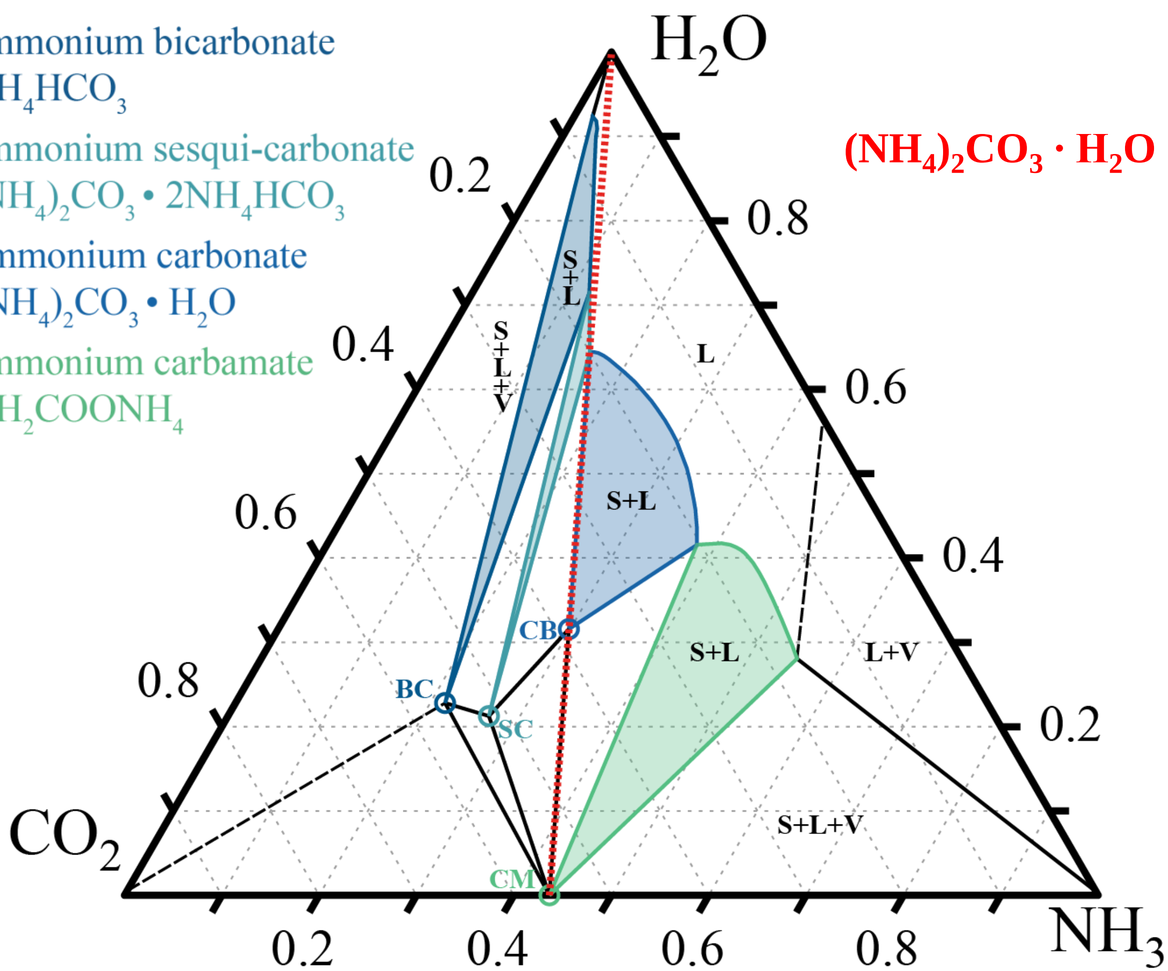

$$(NH_4)_2CO_3 \cdot H_2O \leftrightarrow NH_2COONH_4 + 2H_2O$$

10°C, 1 bar

Ternary phase diagram – Stoichiometry

BC ammonium bicarbonate NH_4HCO_3

SC ammonium sesqui-carbonate $(NH_4)_2CO_3 \cdot 2NH_4HCO_3$

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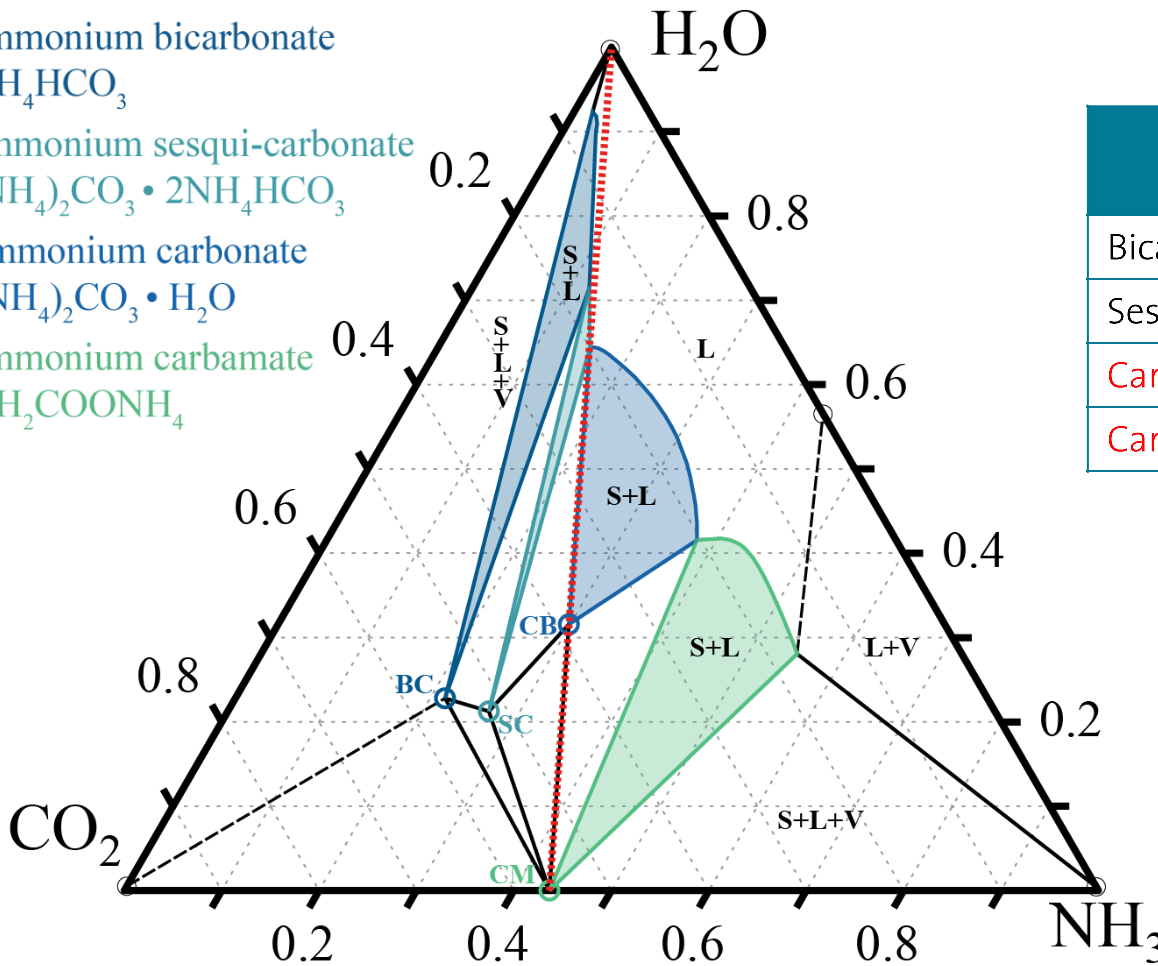

Solid	Molar ratio CO_2/NH_3
Bicarbonate	1/1
Sesqui-carbonate	3/4
Carbonate	1/2
Carbamate	1/2

10°C, 1 bar

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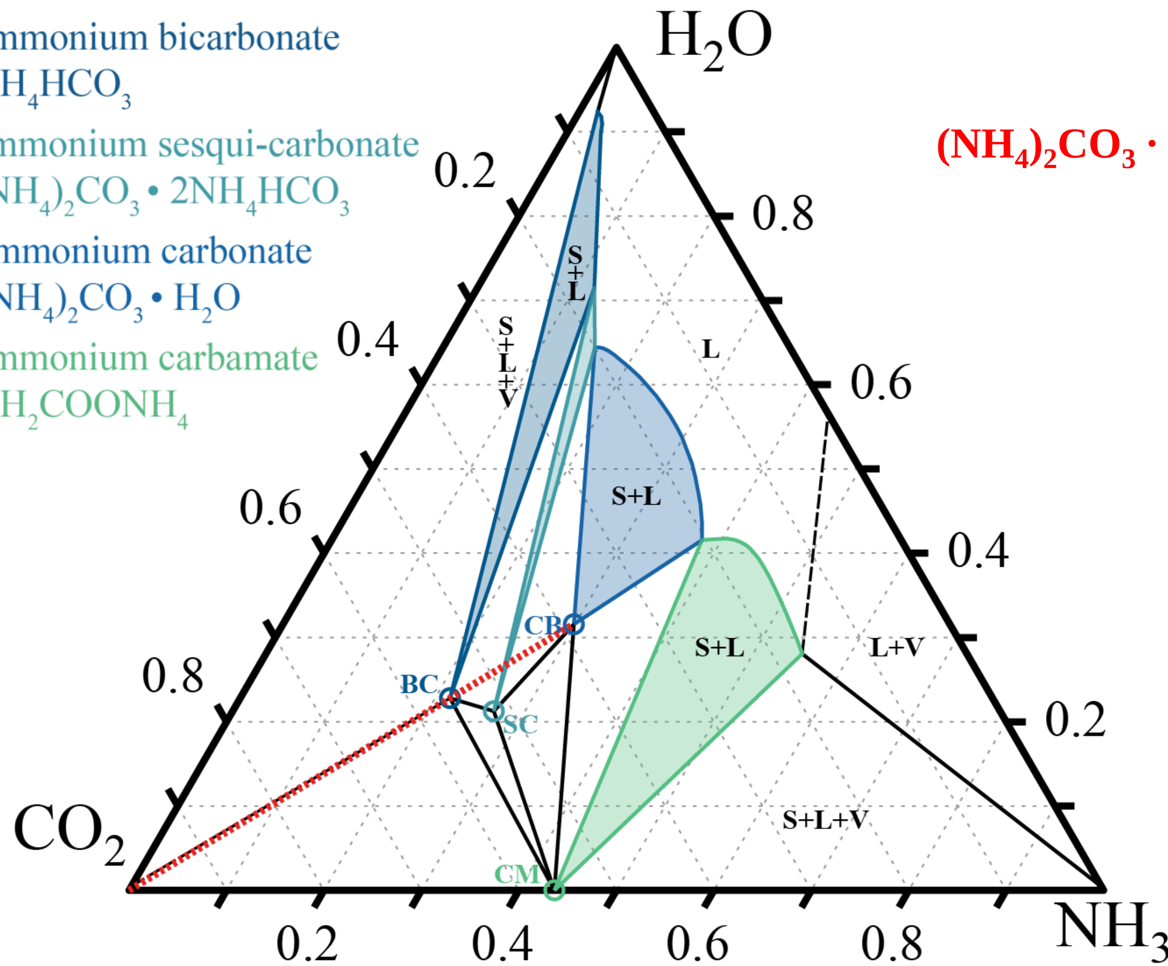

$(NH_4)_2CO_3 \cdot H_2O + CO_2 \leftrightarrow 2NH_4HCO_3$

10°C, 1 bar

Ternary phase diagram – Stoichiometry

BC ammonium bicarbonate NH_4HCO_3

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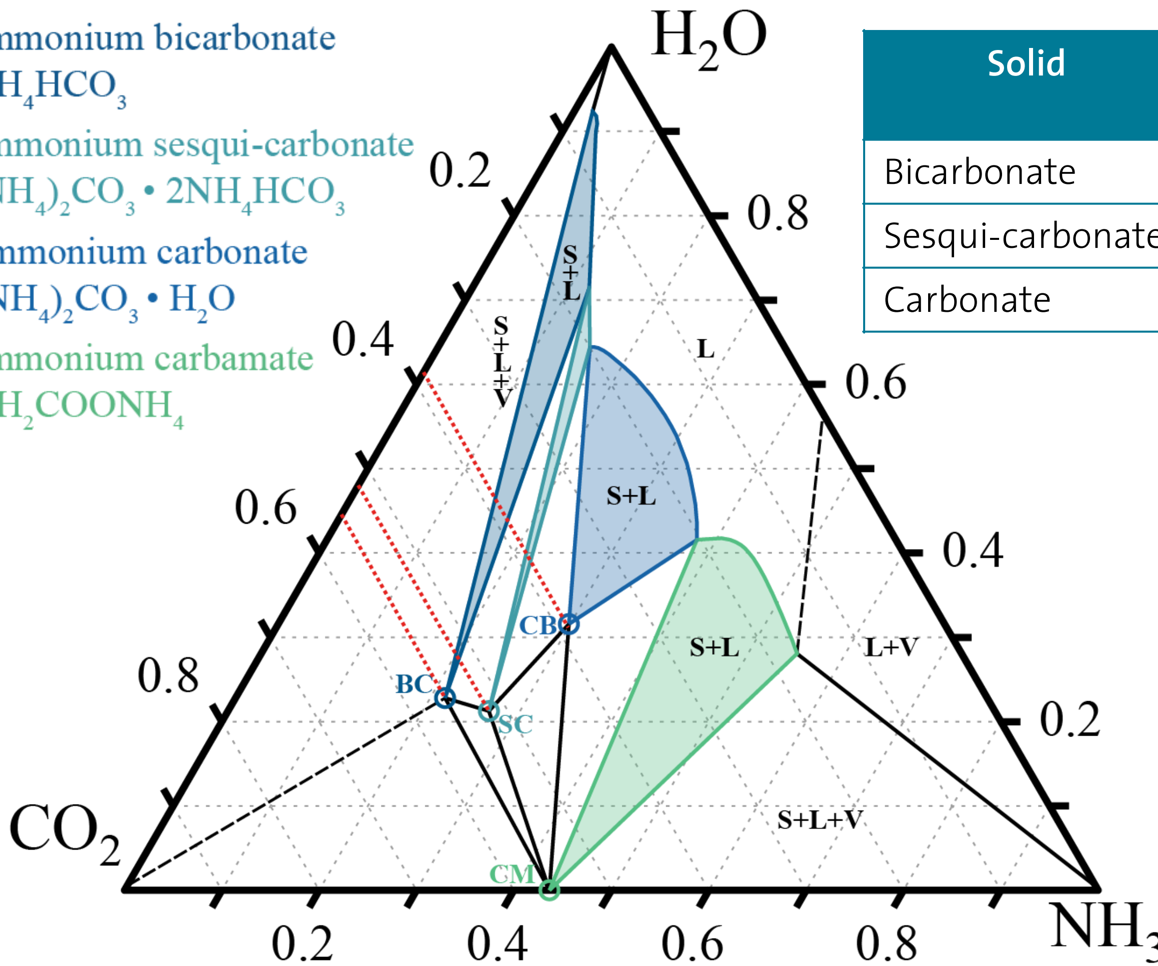


Solid	Molar ratio CO_2/NH_3	Mass fraction of CO_2
Bicarbonate	1/1	0.55
Sesqui-carbonate	3/4	0.52
Carbonate	1/2	0.39

10°C, 1 bar

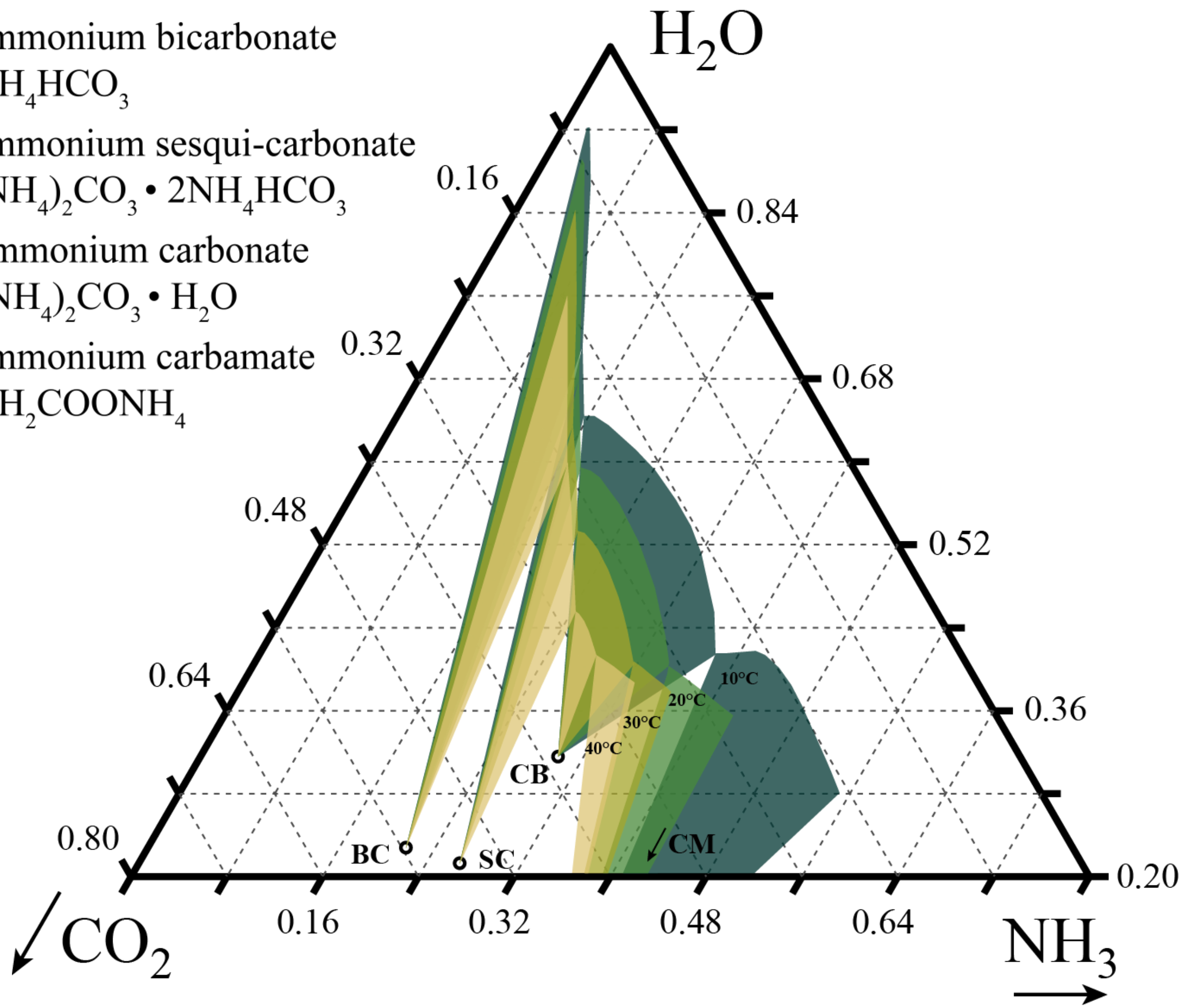
Ternary phase diagram applied to the CAP

BC ammonium bicarbonate NH_4HCO_3

SC ammonium sesqui-carbonate $(NH_4)_2CO_3 \cdot 2NH_4HCO_3$

CB ammonium carbonate $(NH_4)_2CO_3 \cdot H_2O$

CM ammonium carbamate NH_2COONH_4



1 bar

Ternary phase diagram applied to the CAP

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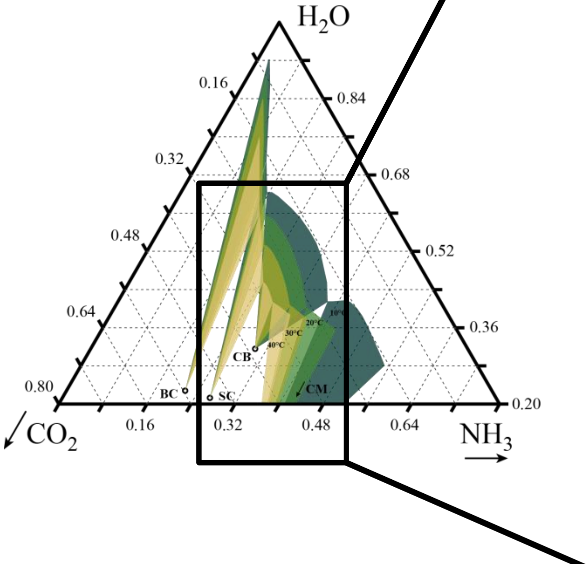

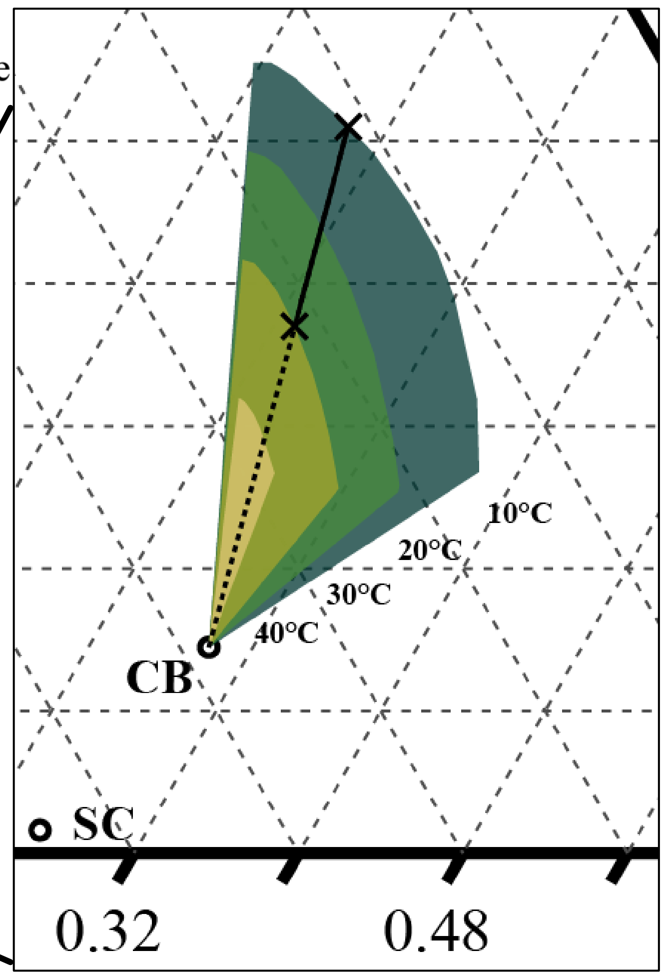

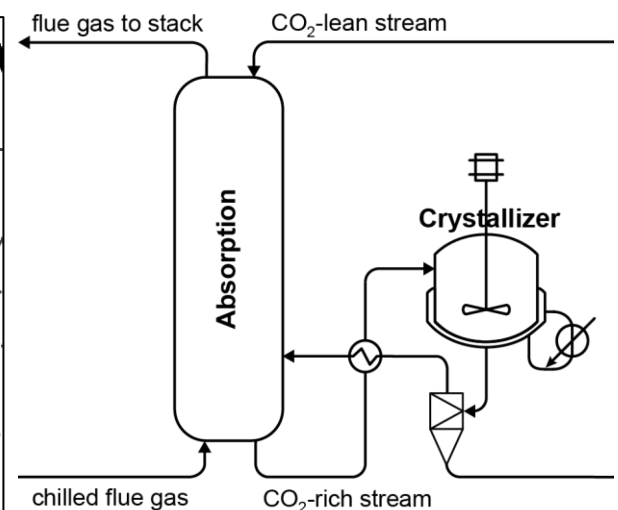

1 bar

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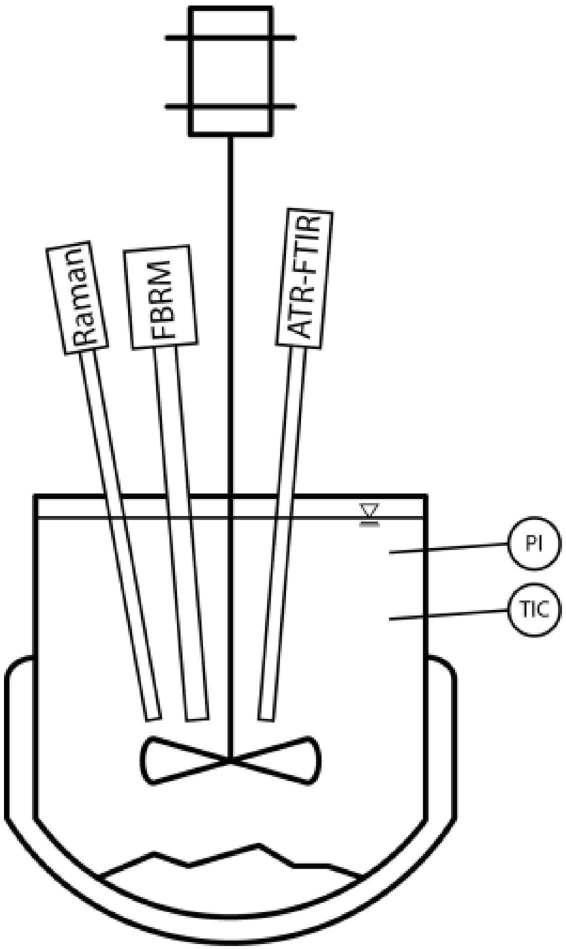
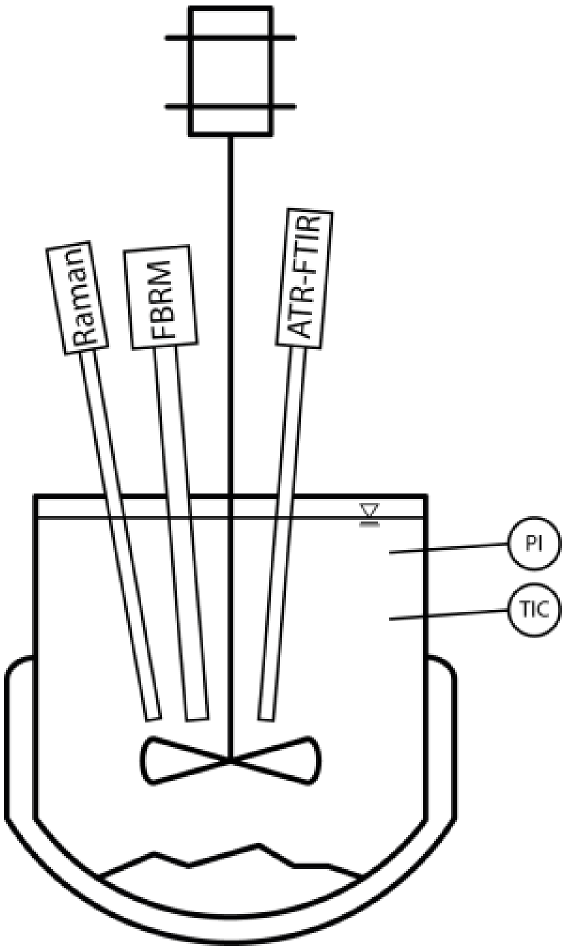
Experimental investigation of crystallization kinetics

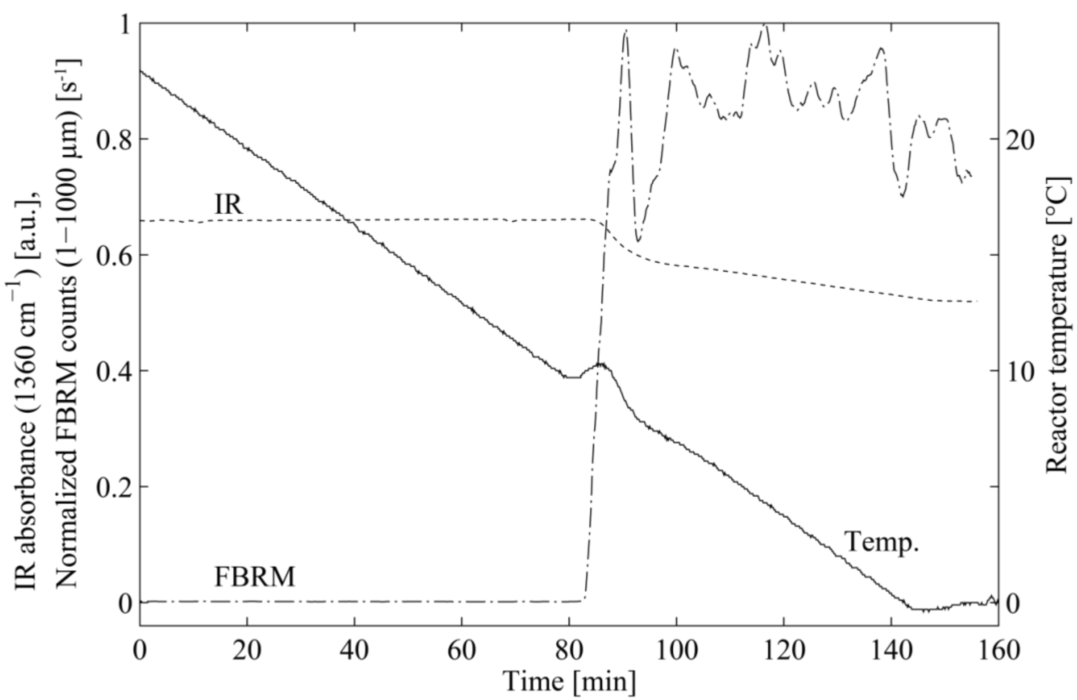


Setup

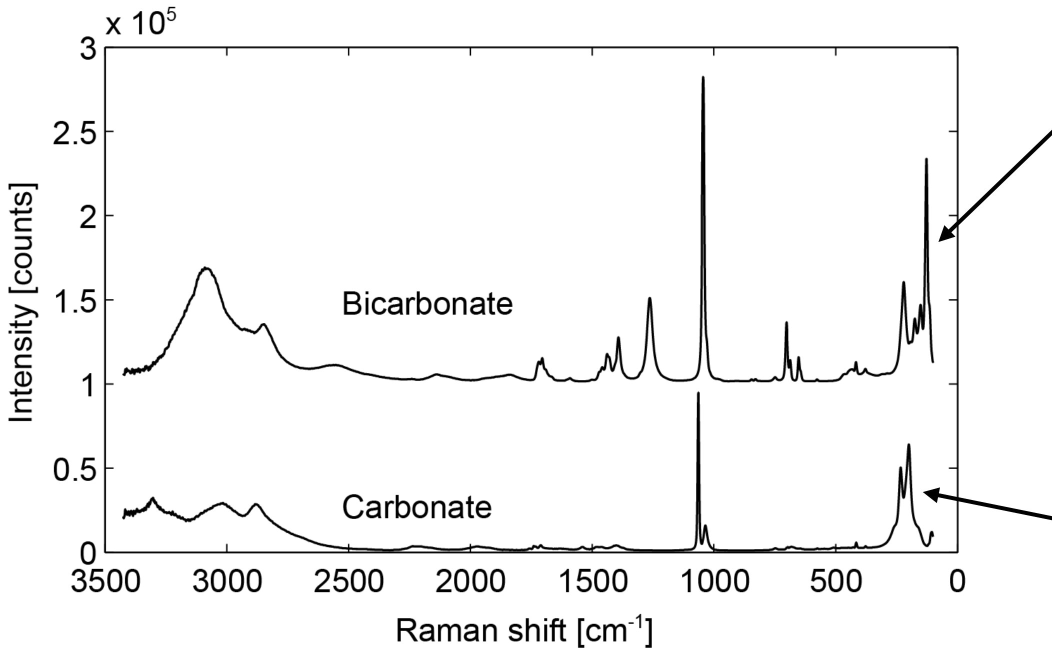
- closed batch system
- minimized gas volume
- **ATR-FTIR** for concentration
- **FBRM** to detect nucleation
- **Raman** for identification of solids

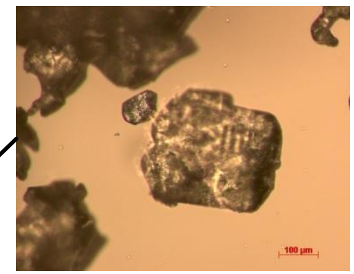
Cooling crystallization experiments

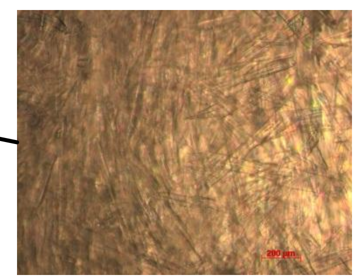


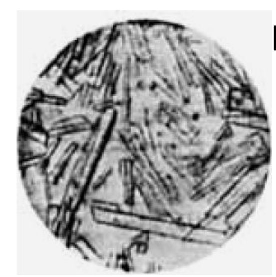


Experimental – Metastable zone width









[3]

[1] RASMIN Web: http://riodb.ibase.aist.go.jp/rasmin/ (2013-09-10)
[2] Veiga et al., 14th International Symposium on Industrial Crystallization (ISIC) 1999
[3] Guyer & Piechowicz, *Helv. Chim. Acta*, 27 (1943) 858-67

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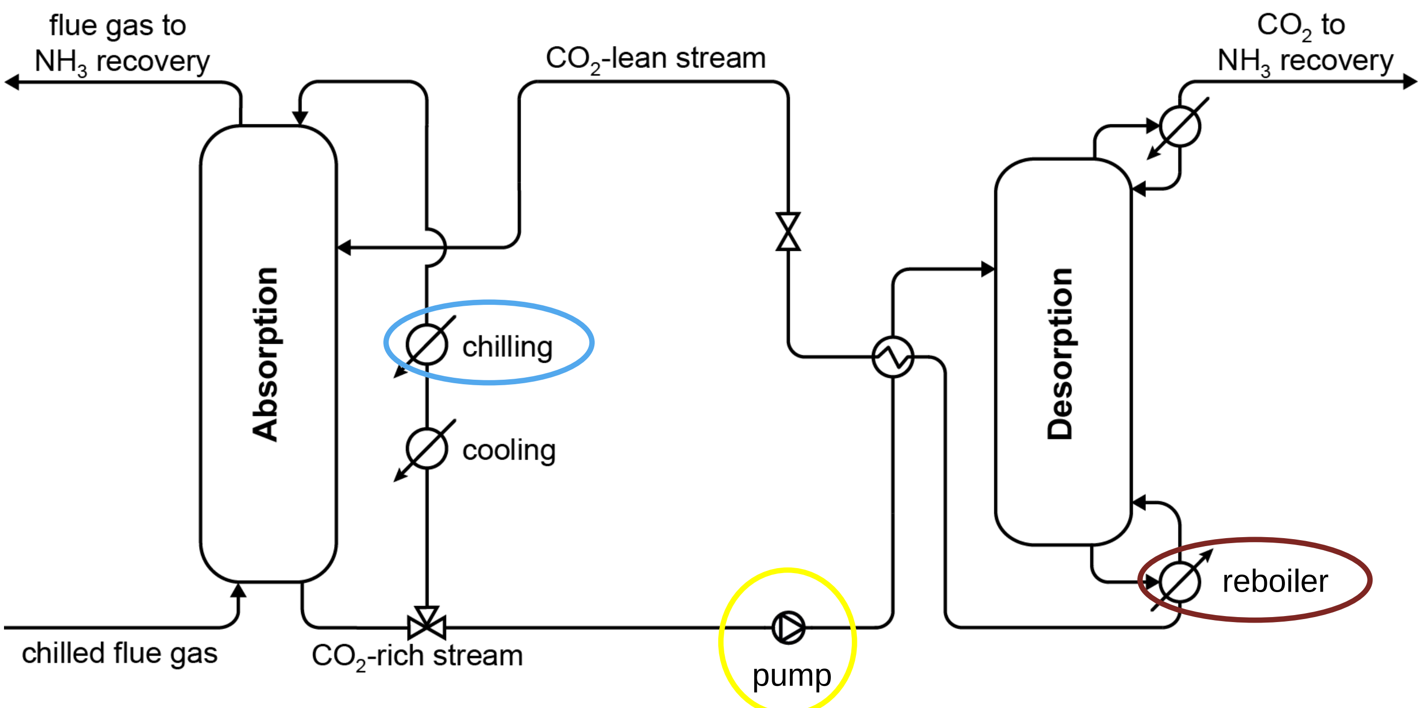
Process simulations

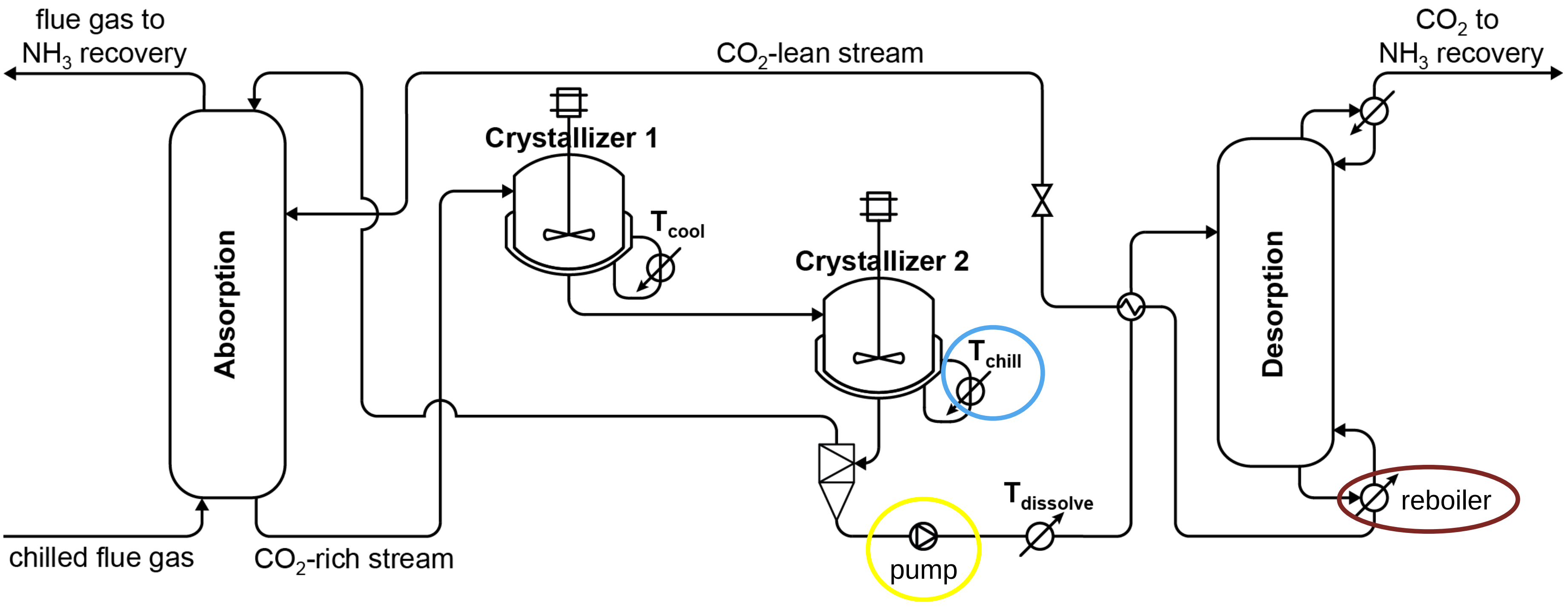
- A) Standard CAP (solid-free)



Gal (2006), WO 2006/022885 A1
Black et al. (2013), US 2013/0028807 A1

Process simulations

- B) Crystallizer-CAP



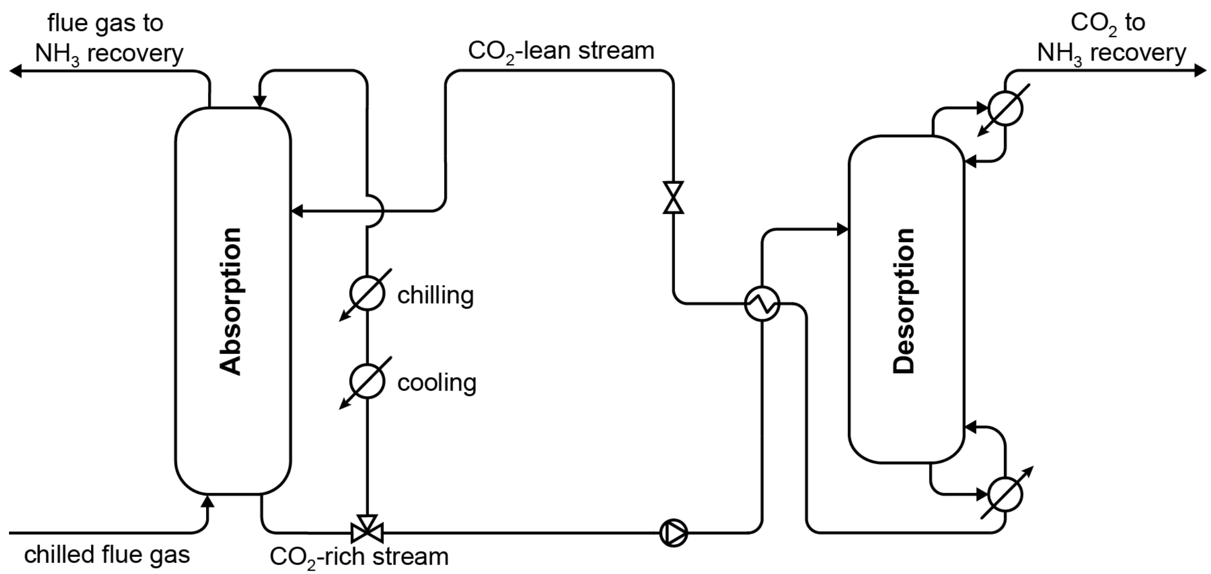
Black et al. (2013), US 2013/0028807 A1

Process simulations – Methods

- Implementation of Extended UNIQUAC model in Aspen Plus [1,2]
- Absorber
  - Radfrac
  - 30/50 stages
- Desorber
  - Radfrac
  - 10 equilibrium stages
  - 10 bar
- Crystallizer
  - CSTR
  - equilibrium-based
- benchmarked against simulations published by Thomsen group [1,2]

[1] Darde et al., *Int J Greenh Gas Con* 8 (2012) 61-72
[2] Darde et al., *Int J Greenh Gas Con* 10 (2012) 74-87

Same specifications for both processes



Absorber

- Flue gas inlet conditions
- Lean stream conditions
- CO_2 capture rate (~90%)
- NH_3 slip before ammonia recovery

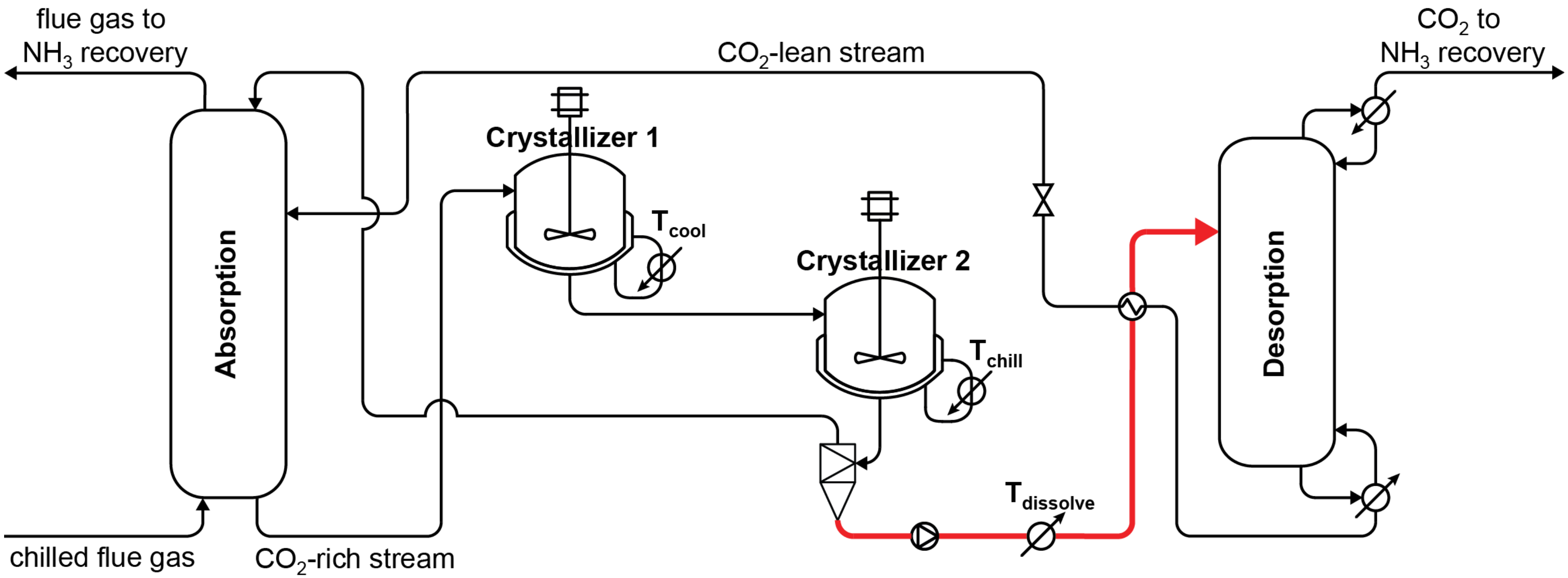
Desorber

- Pressure
- Vapor fraction of feed
- CO_2 purity

General parameters

- ΔT for heat exchange (3°C)
- Utilities:
  - cooling water at 15°C,
  - chilling water at 2°C

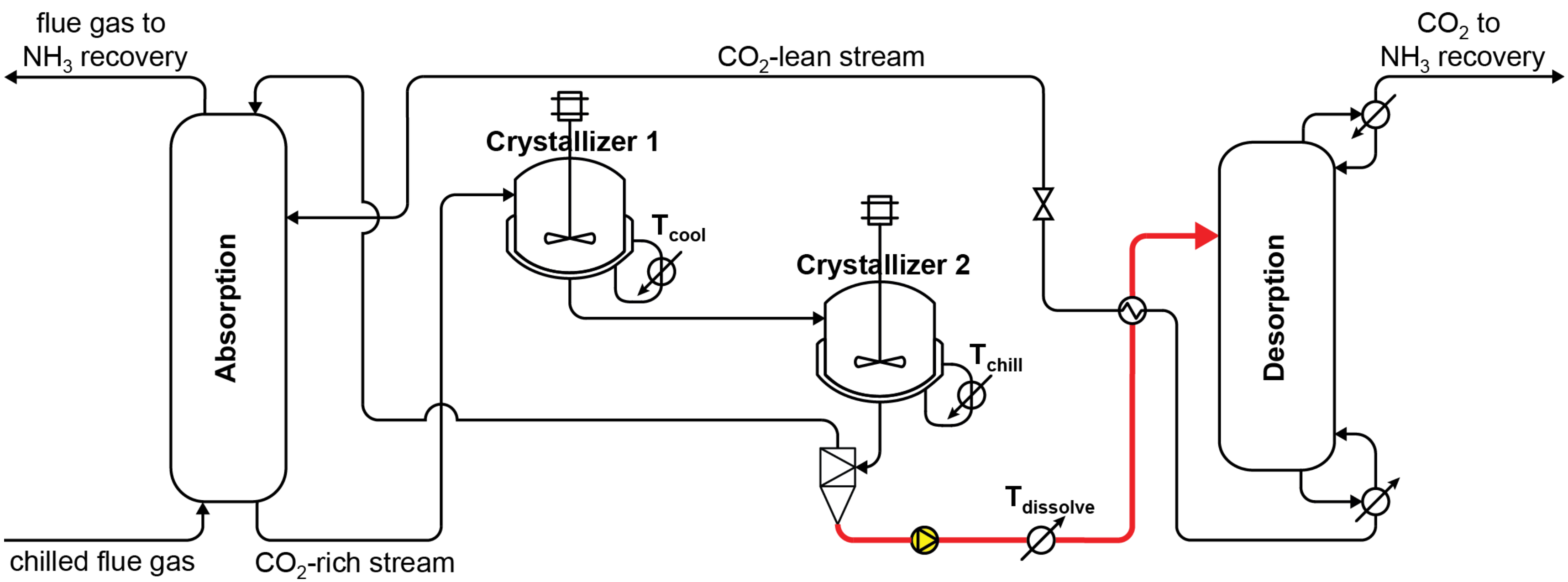
Simulation results - Comparison



Stream to regeneration

Solid density (wt.-%)	14%
CO_2 loading (mol CO_2/mol NH_3)	+ 27%
Mass flow (kg/s)	- 40%

Simulation results - Comparison



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Energy penalty «key players»

Pump power (MW_{el})	- 49%

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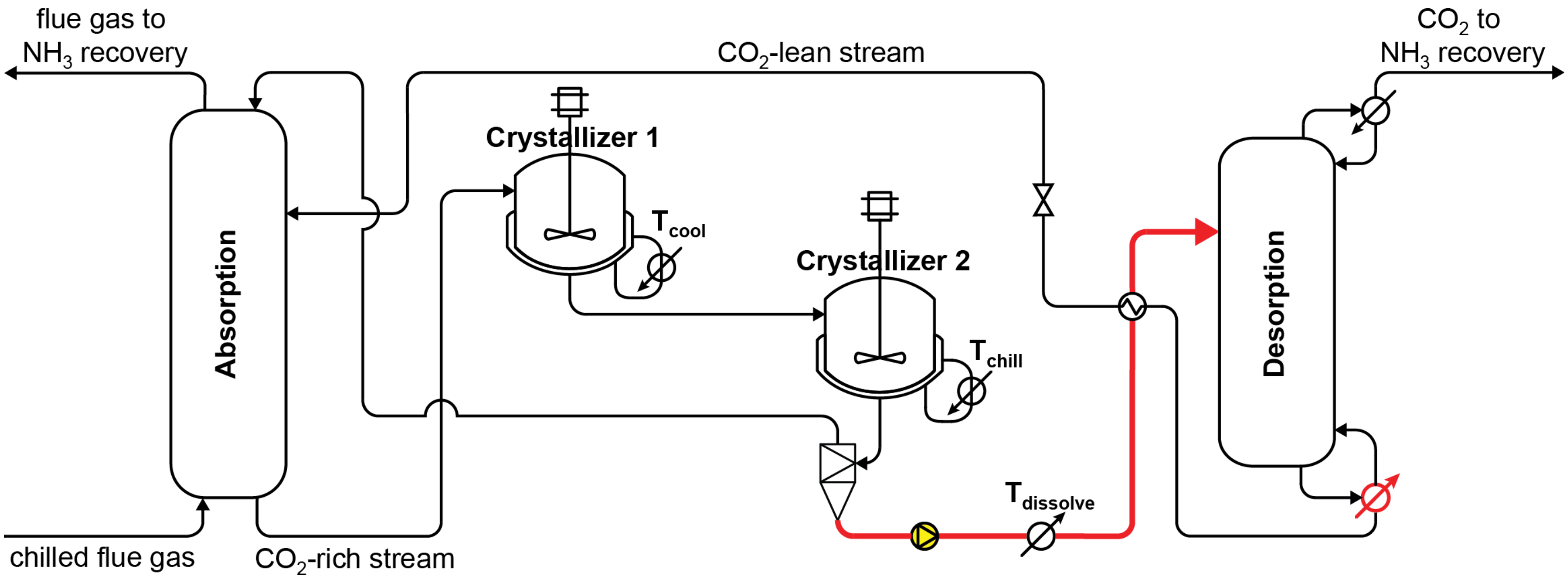

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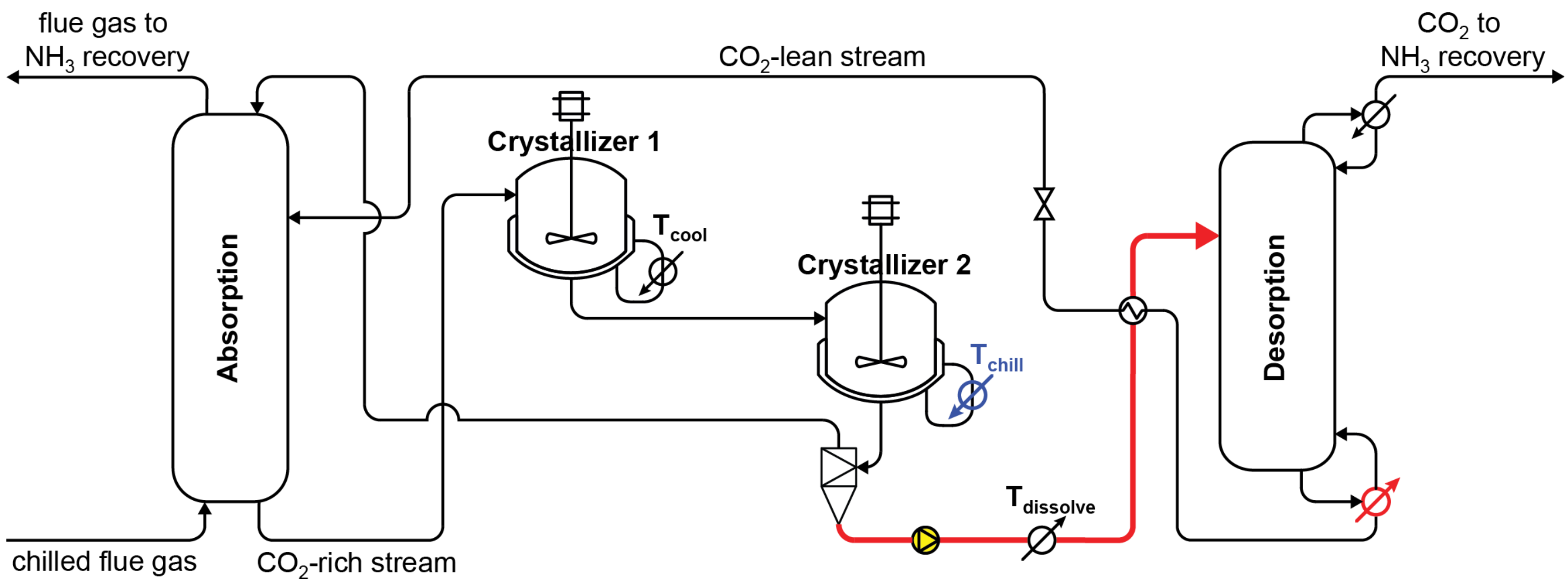
Reboiler duty (MW_{th})	- 20%

Simulation results - Comparison



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Energy penalty «key players»

Pump power (MW_{el})	- 49%
Reboiler duty (MW_{th})	- 20%
Chilling duty (MW_{th})	+ 200%

Comparison on the basis of electric energy

Pump power (MW$_{el}$) ⇨ Pump efficiency $\eta_P = 0.75$ ⇨ $\dot{W}_{el} = \frac{\dot{W}_{el}^{ideal}}{0.75}$

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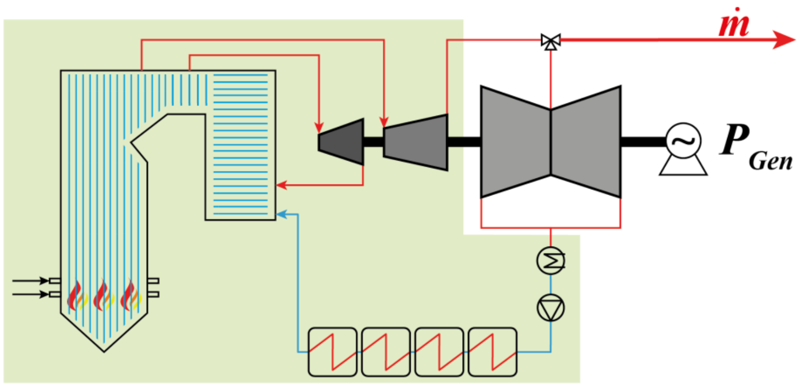
Pump power (MW$_{el}$) → Pump efficiency $\eta_P = 0.75$ → $\dot{W}_{el} = \frac{\dot{W}_{el}^{ideal}}{0.75}$

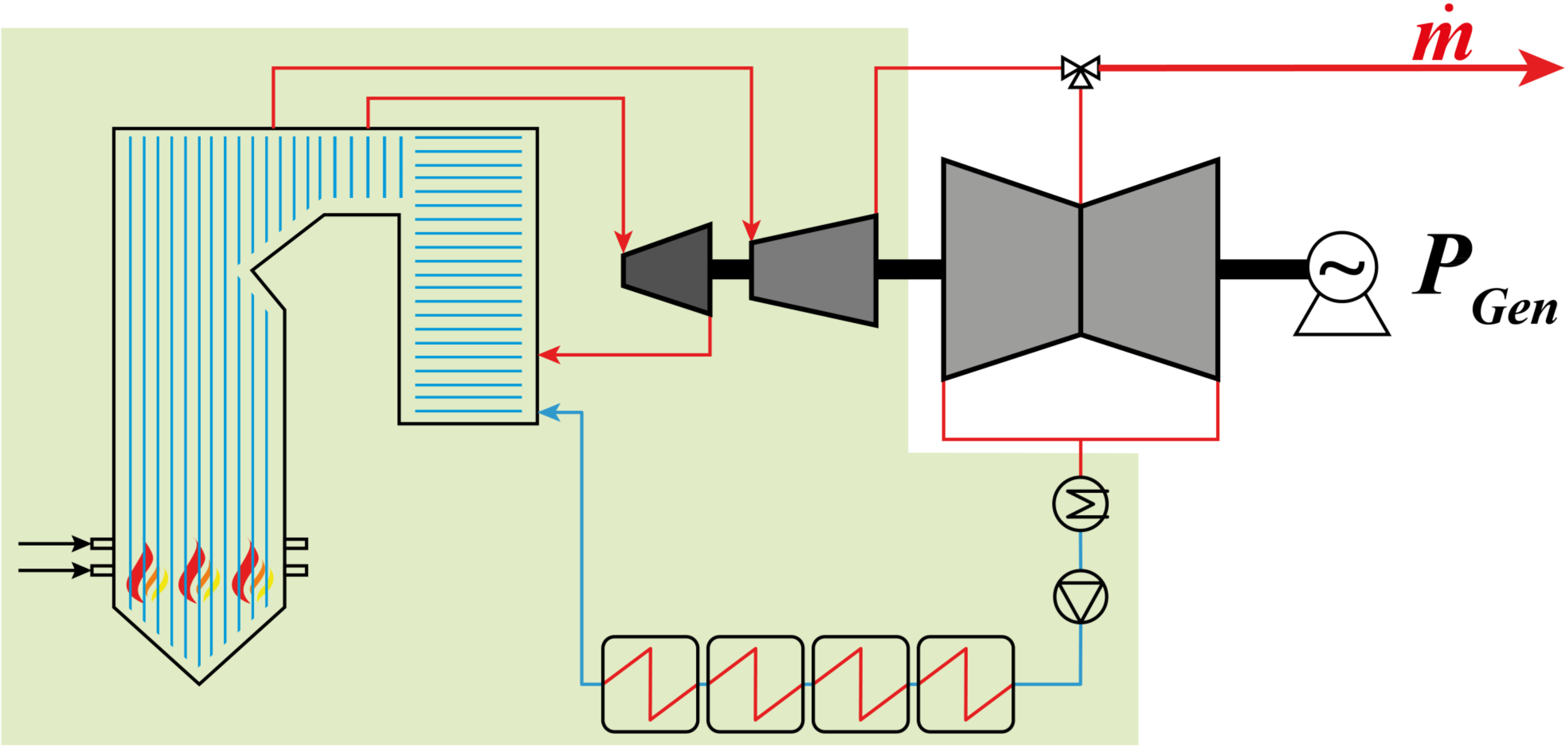
ΔP_{Gen} due to steam bleeding

Reboiler duty (MW$_{th}$)



European Benchmarking Task Force (2011) CAESAR Project, No. 213206

Comparison on the basis of electric energy



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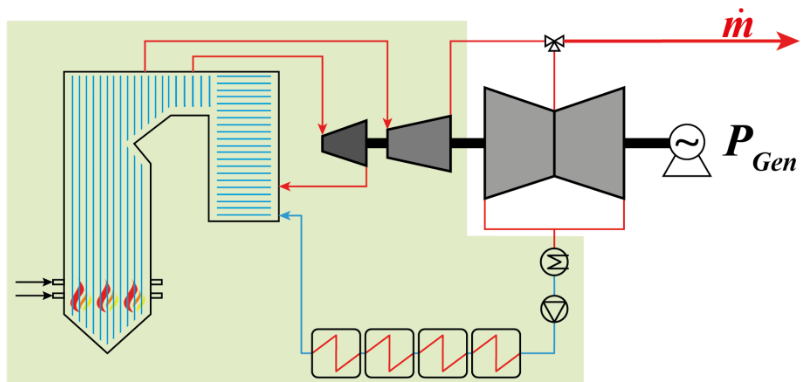
Reboiler duty (MW$_{th}$)



European Benchmarking Task Force (2011) CAESAR Project, No. 213206

$$\dot{W}_{el} = P_{Gen}^{0} - P_{Gen}^{w/bleed}$$

Chilling duty (MW$_{th}$)

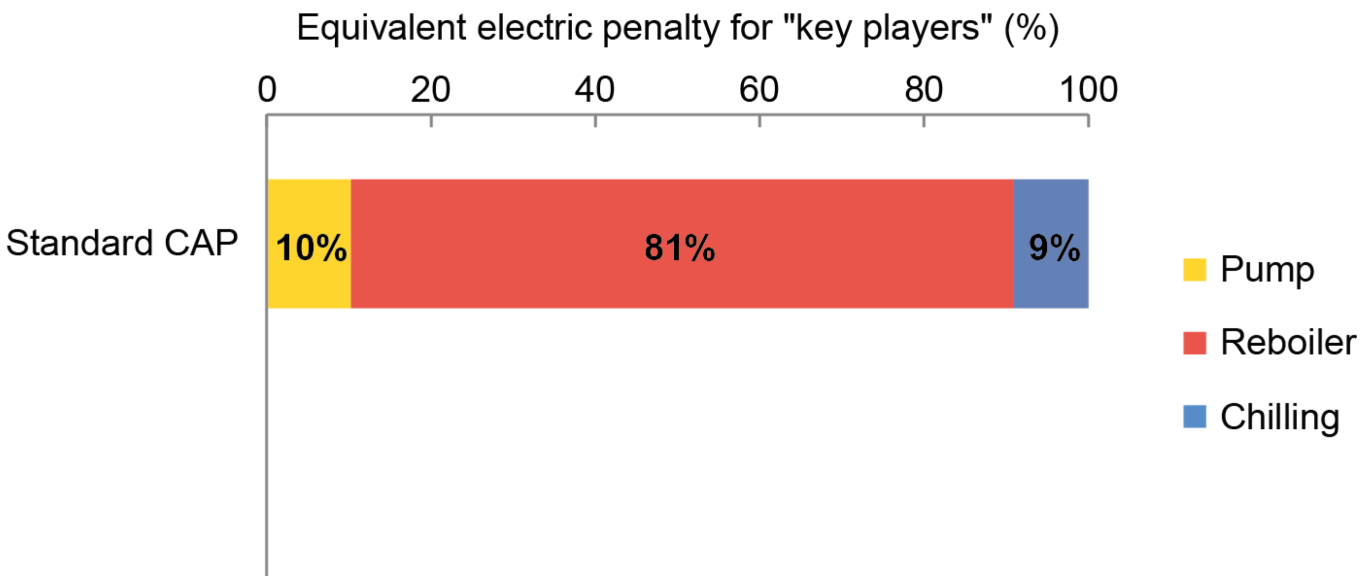
Coefficient of performance (COP)

$$\mathrm{COP_{ideal}} = \frac{T_c}{T_h - T_c} = \frac{275\,\mathrm{K}}{(298-275)\,\mathrm{K}} = 12.0$$

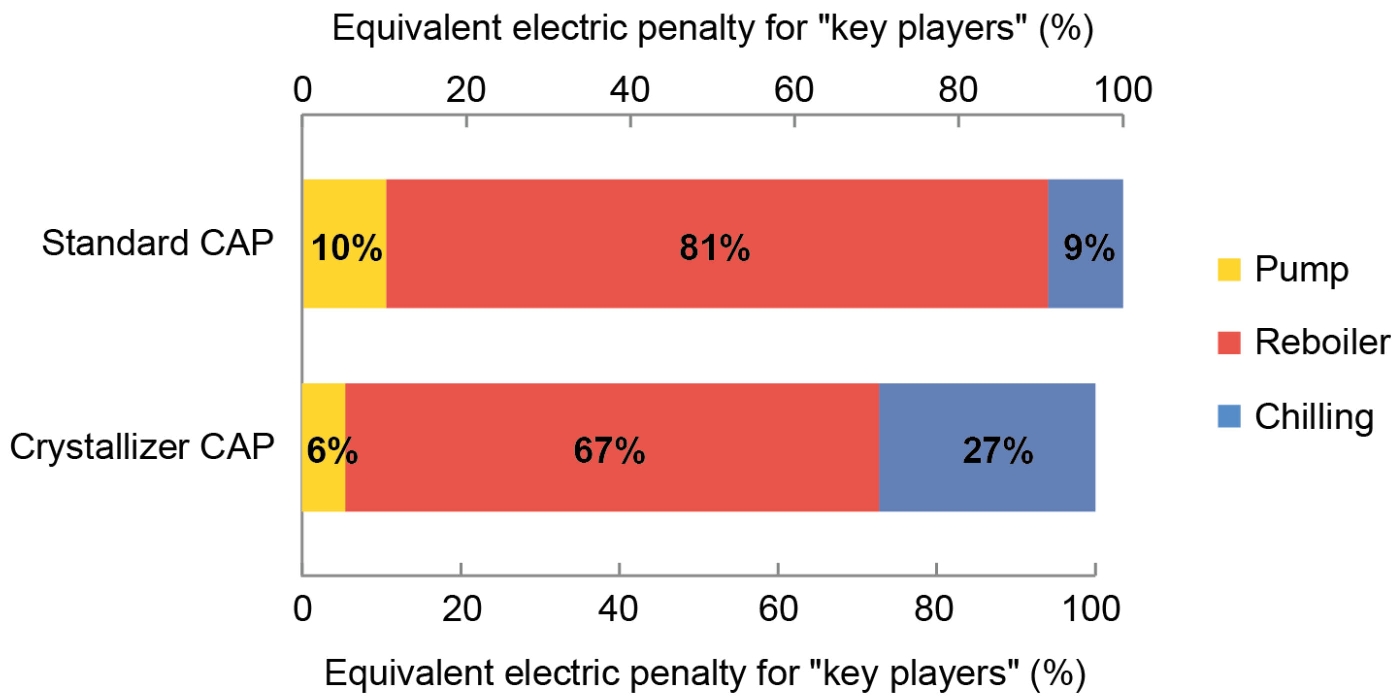
$$\mathrm{COP} = 0.6\,\mathrm{COP_{ideal}} = 7.2$$

$$\dot{W}_{el} = \frac{\dot{Q}_{chill}}{\mathrm{COP}}$$

Comparison on the basis of electric energy



Comparison based on energy penalty



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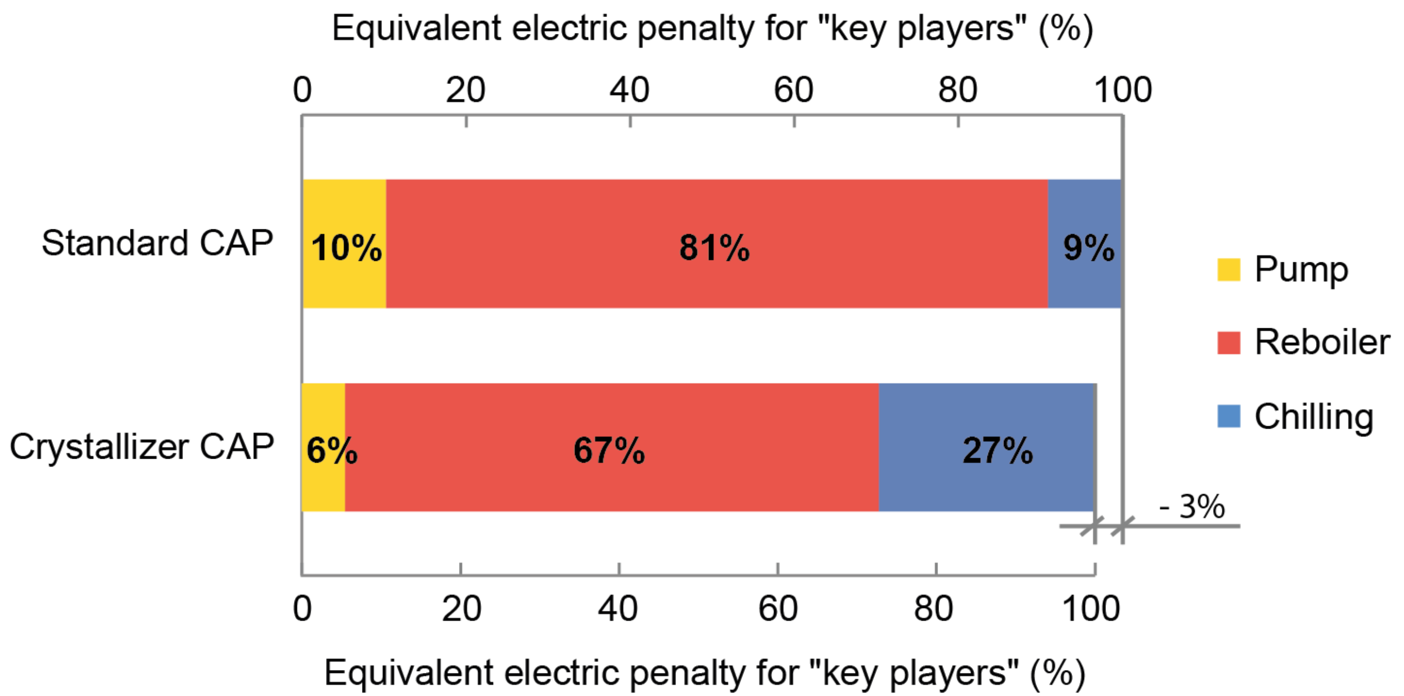

- Both processes not fully optimized
- Potential for heat integration for solid-mode

Conclusions

- Ternary phase diagrams as a tool for the design of a solid-mode CAP
- Experimental investigation of solid formation in the CO_2-NH_3-H_2O system
  - Setup and analytical concept
  - On-line identification of solids by RAMAN
- Process simulation of solid-mode CAP
  - Significant reduction of the reboiler duty (approx. 20%)
  - Slight reduction of overall energy penalty (based on «key players»)
  - Potential for further reduction with heat integration
  - Increase of complexity and CAPEX for absorption section (low pressure)
  - Decrease of size and CAPEX for regeneration section (high pressure)