ECRA-Cemcap Workshop

Chilled ammonia process for CO_2 capture

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Matteo Gazzani
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Presentation layout

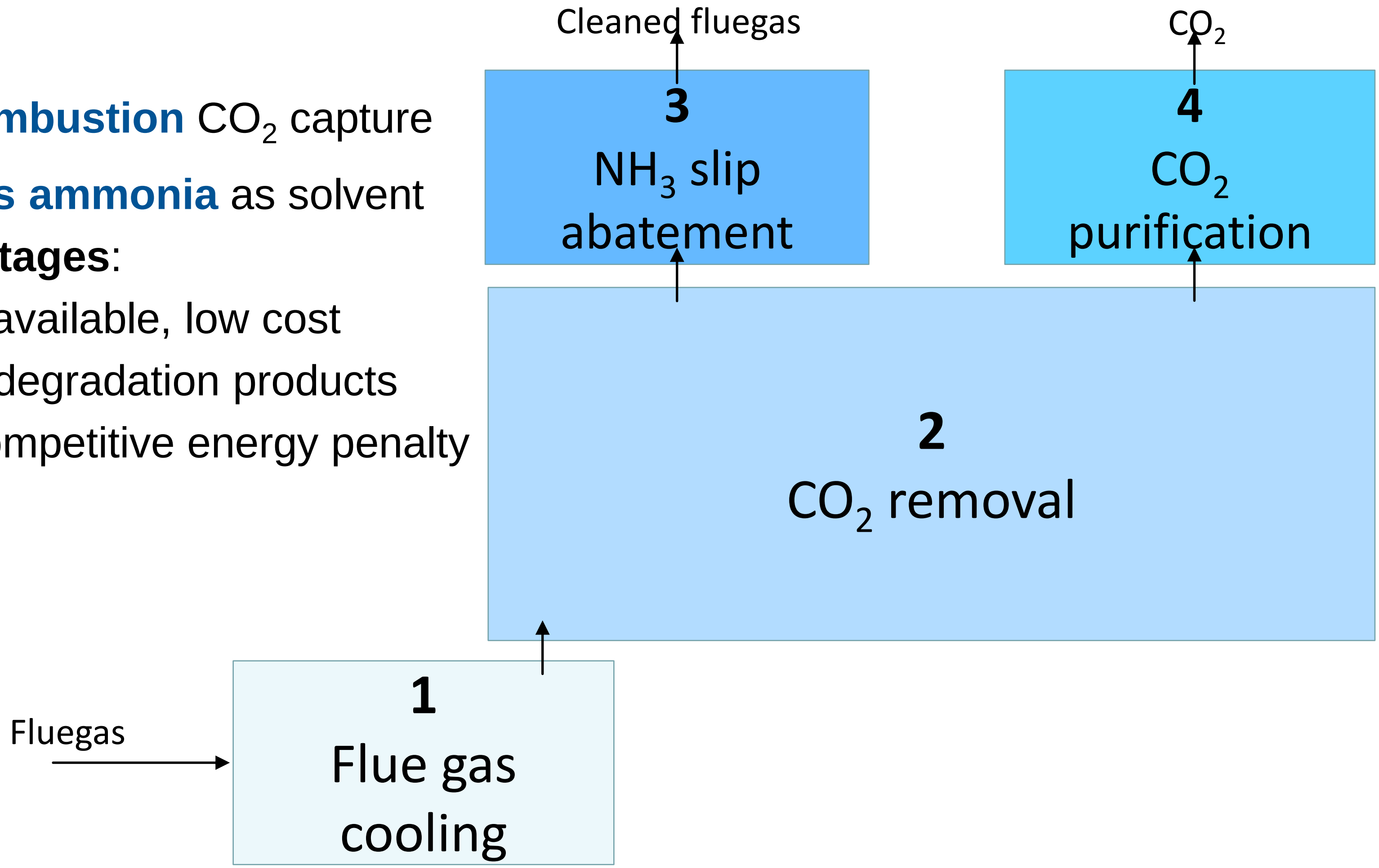
1. Introduction to Chilled Ammonia Capture Process (CAP)
2. Research topics in the CAP
3. Criticalities for CAP application to cement plant conditions

The Chilled Ammonia Process

- **Post-combustion** CO_2 capture
- **Aqueous ammonia** as solvent

Main advantages:

- ✓ globally available, low cost
- ✓ no toxic degradation products
- ✓ highly competitive energy penalty



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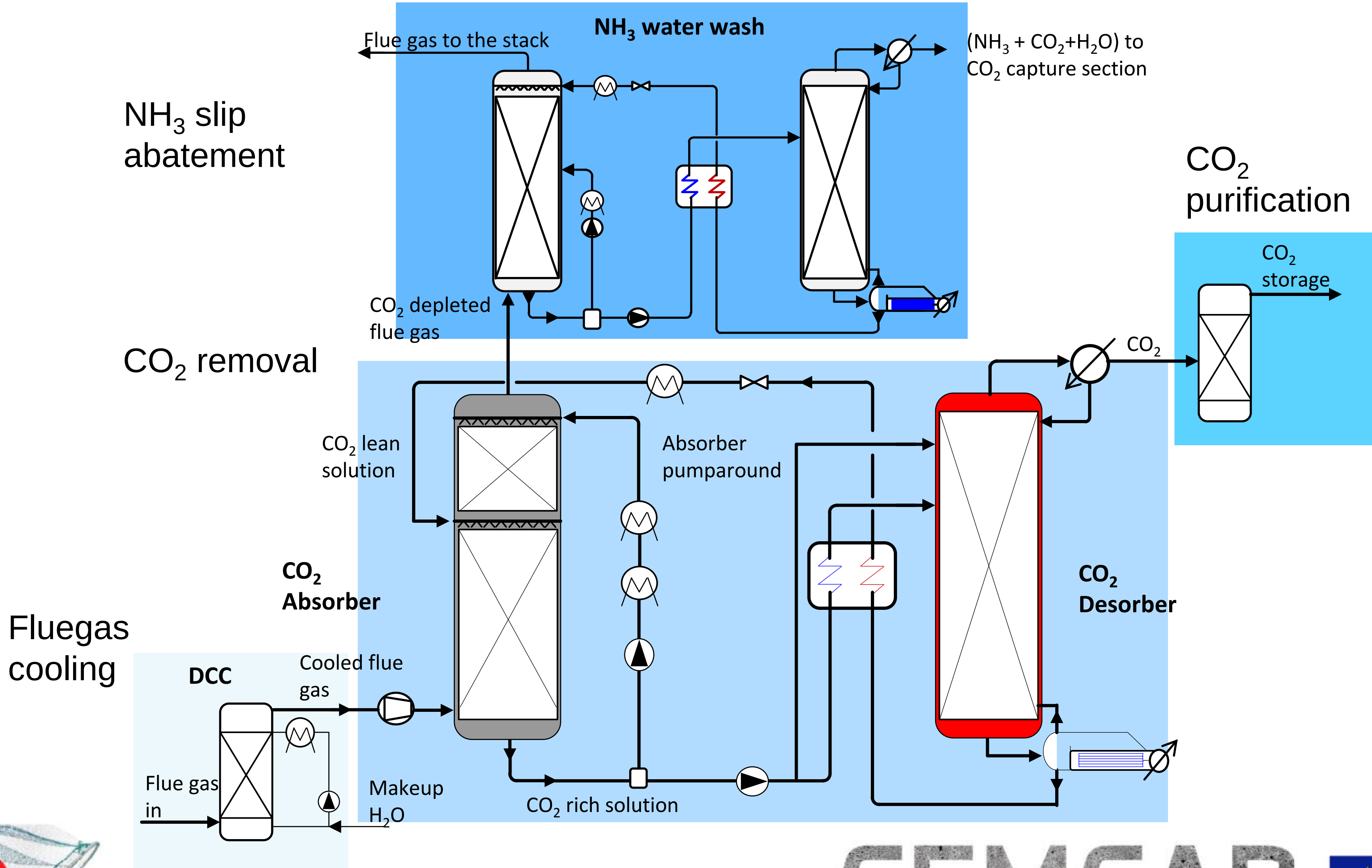
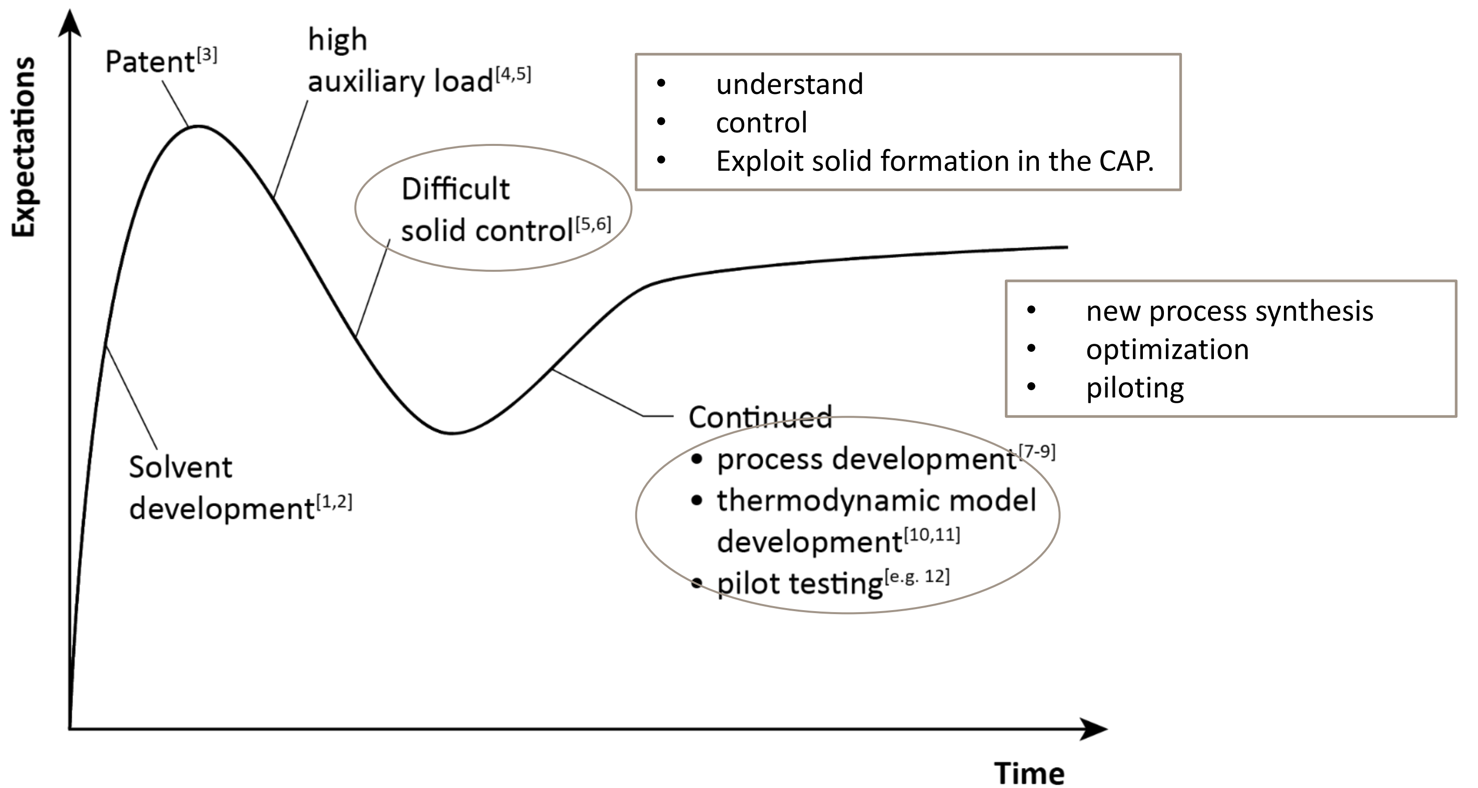
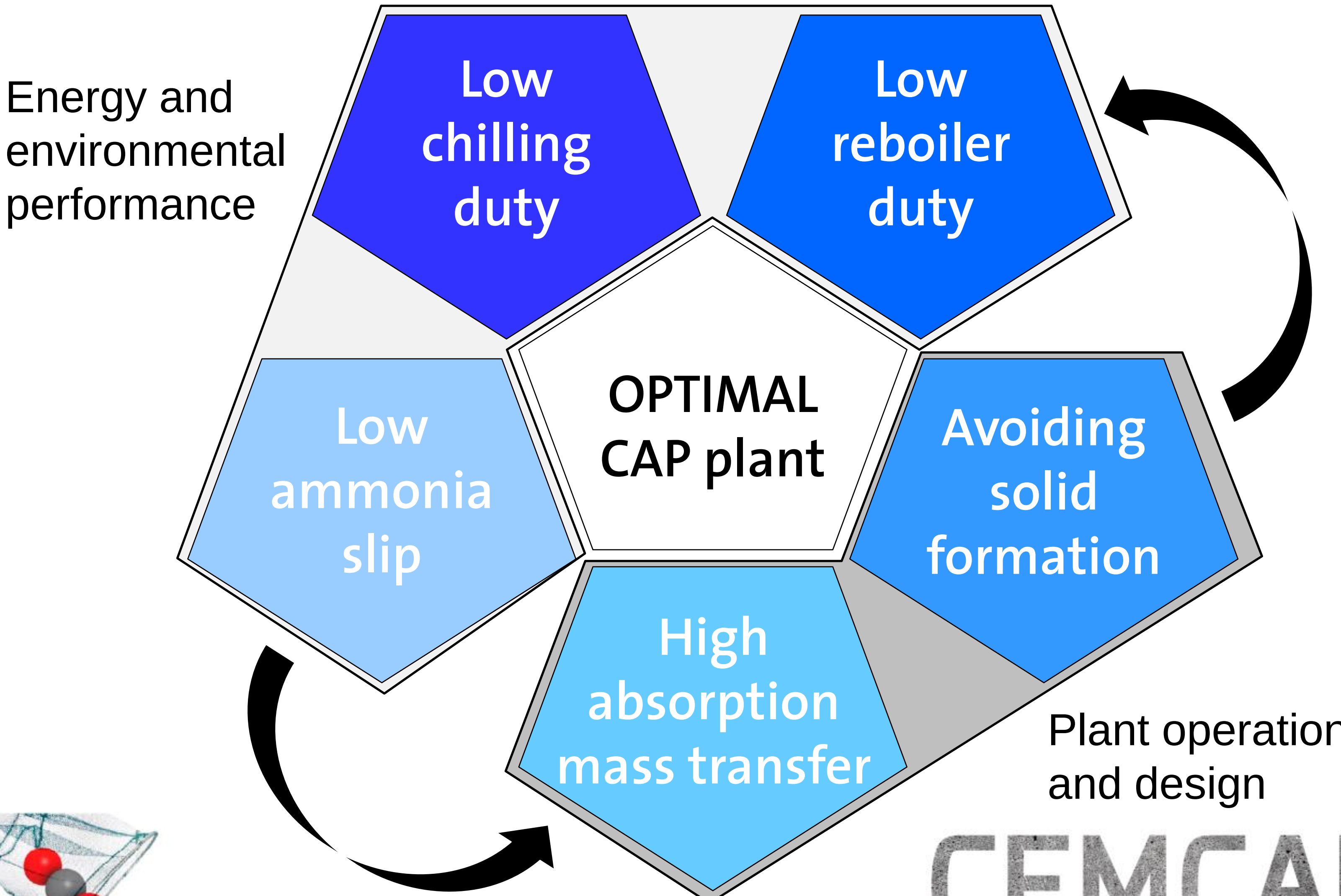


Hype cycle for NH_3-based CO_2 capture



[1] Bai and Yeh. *Ind Eng Chem Sc.* 36 (1997) 2490-2493
[2] Bai and Yeh. *Sci Total Environ.* 228 (1999) 121-133
[3] Gal. (2006) Patent No. WO2006/022885A1
[4] Mathias et al. *Energy Procedia* 1 (2009) 1227-1234
[5] Mathias et al. *Int J Greenh Gas Con* 4 (2010) 174-179
[6] Yu et al. *Chem Eng Res and Des.* 89 (2011) 1204-1215
[7] Bollinger et al. Alstom Technical Report, Paper No. 72
[8] Darde et al. *Int J Greenh Gas Control*, 10 (2012) 74-87
[9] Black et al. (2013) Patent No. US 2013/0028807 A1
[10] Darde et al. *Ind Eng Chem Res.* 49 (2010) 12663-12674)
[11] Que and Chen. *Ind Eng Chem Res*. 50 (2011) 11406-11421
[12] Baburao et al. Presentation at TCCS-8, Trondheim, Norway

Features of an efficient Chilled Ammonia Process



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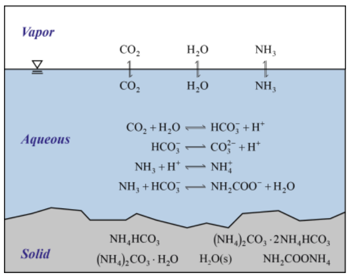
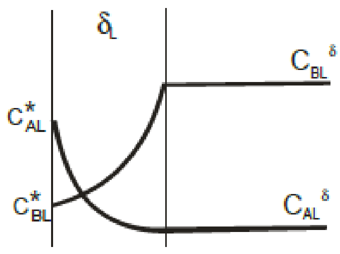
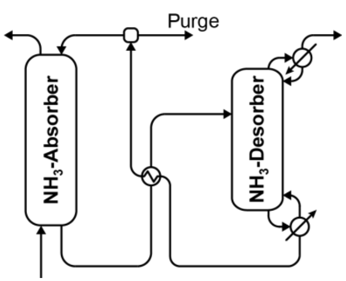
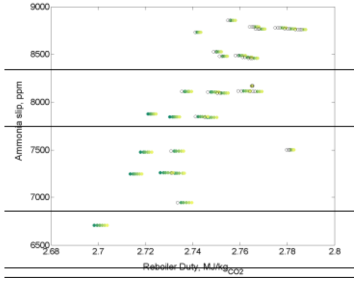
CAP research topics

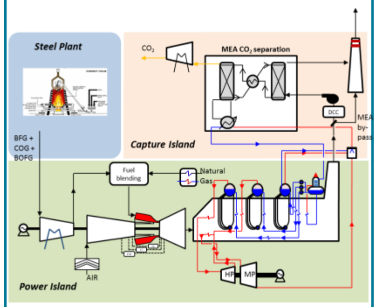
Thermo-dynamics	Kinetics	Process Synthesis	Process Optimization	Process Integration

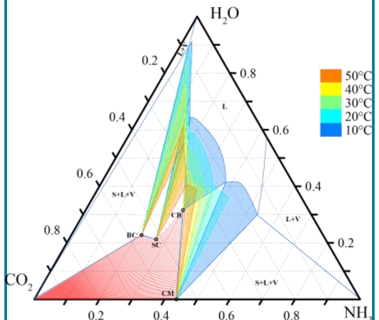


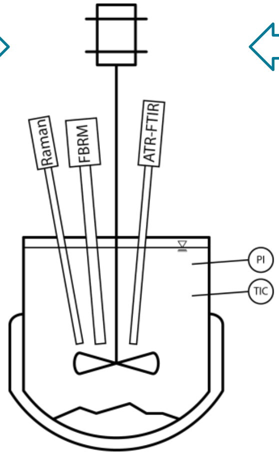


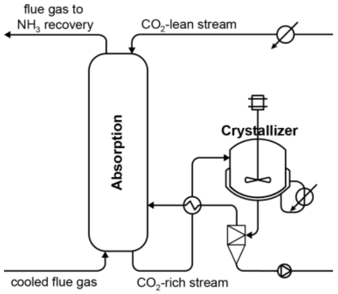


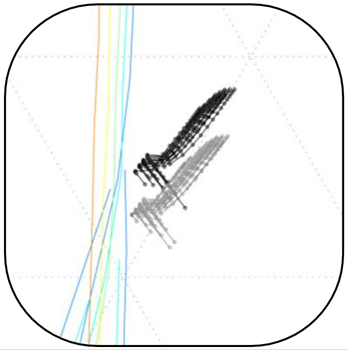












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POWER PRODUCTION	
Gas turbine*, MW_{el}	204.1
Steam turbine, MW_{el}	62.4
CONSUMPTIONS	
Steam cycle pumps, MW_{el}	1.5
CO2 compressor, MWel	17.5
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Balance of Plant, MW_{el}	0.2
BALANCE	
Net Power Output, MW_{el}	240.1
Net Electric Efficiency, $\%_{LHV}$	**41.62**
CO_2 specific emissions, g/kWh_{el}	293.0
Avoided CO_2, %	**65.6**
SPECCA, MJ_{LHV}/kg_{CO2}	**3.76**

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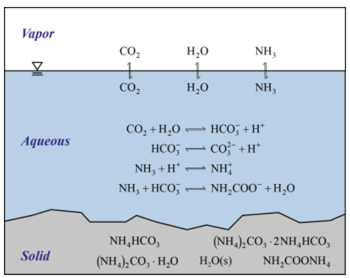

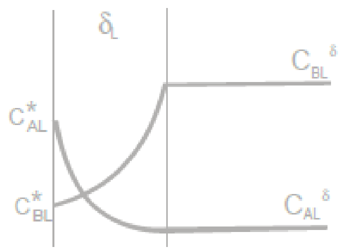

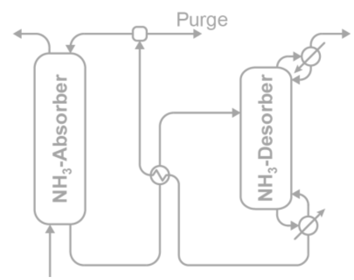

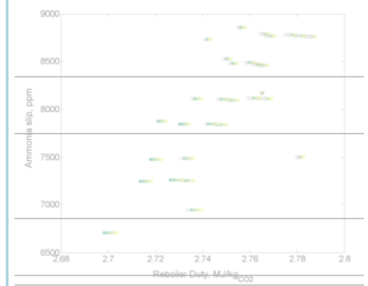

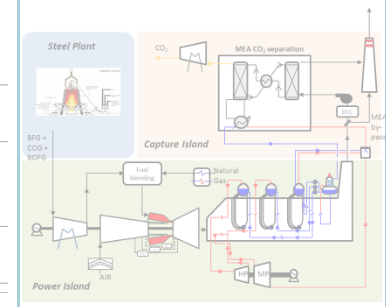

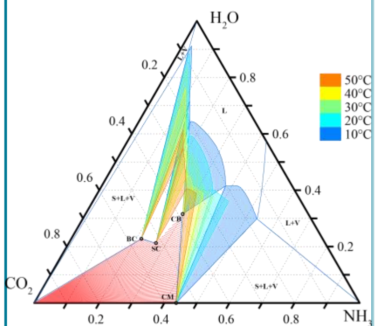

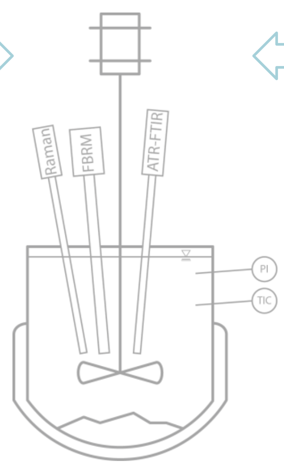

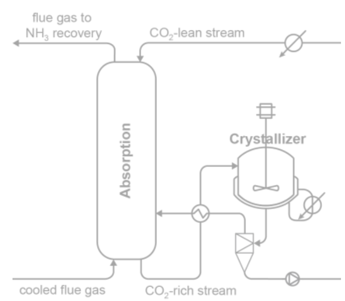

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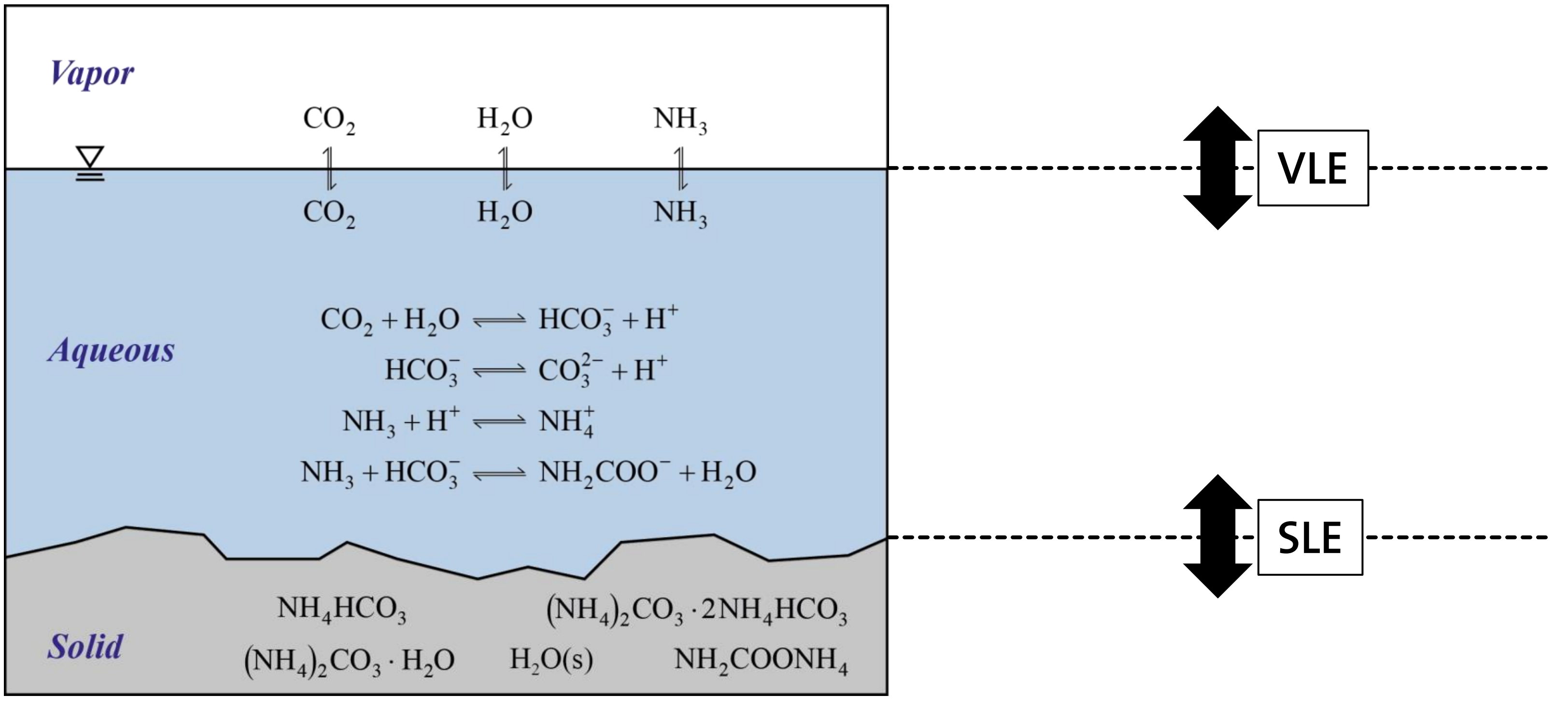
Understanding the system thermodynamics



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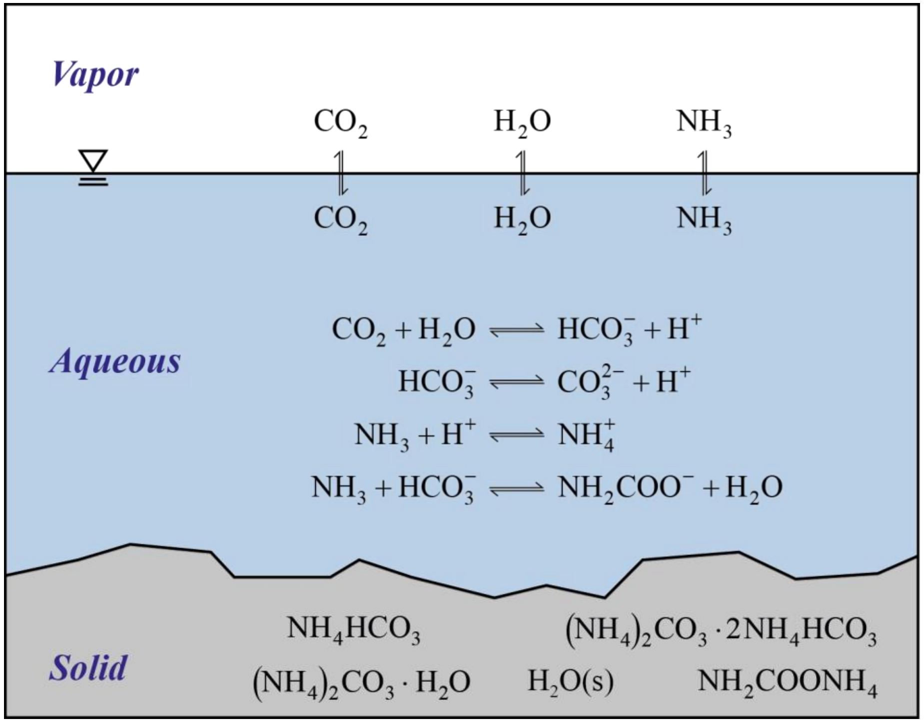
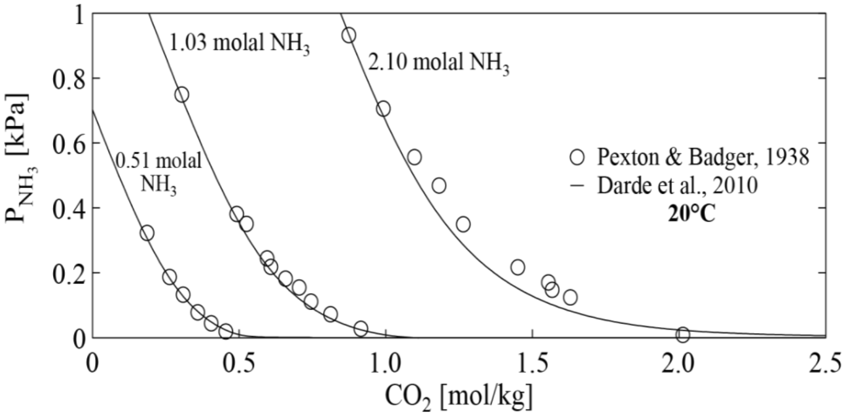
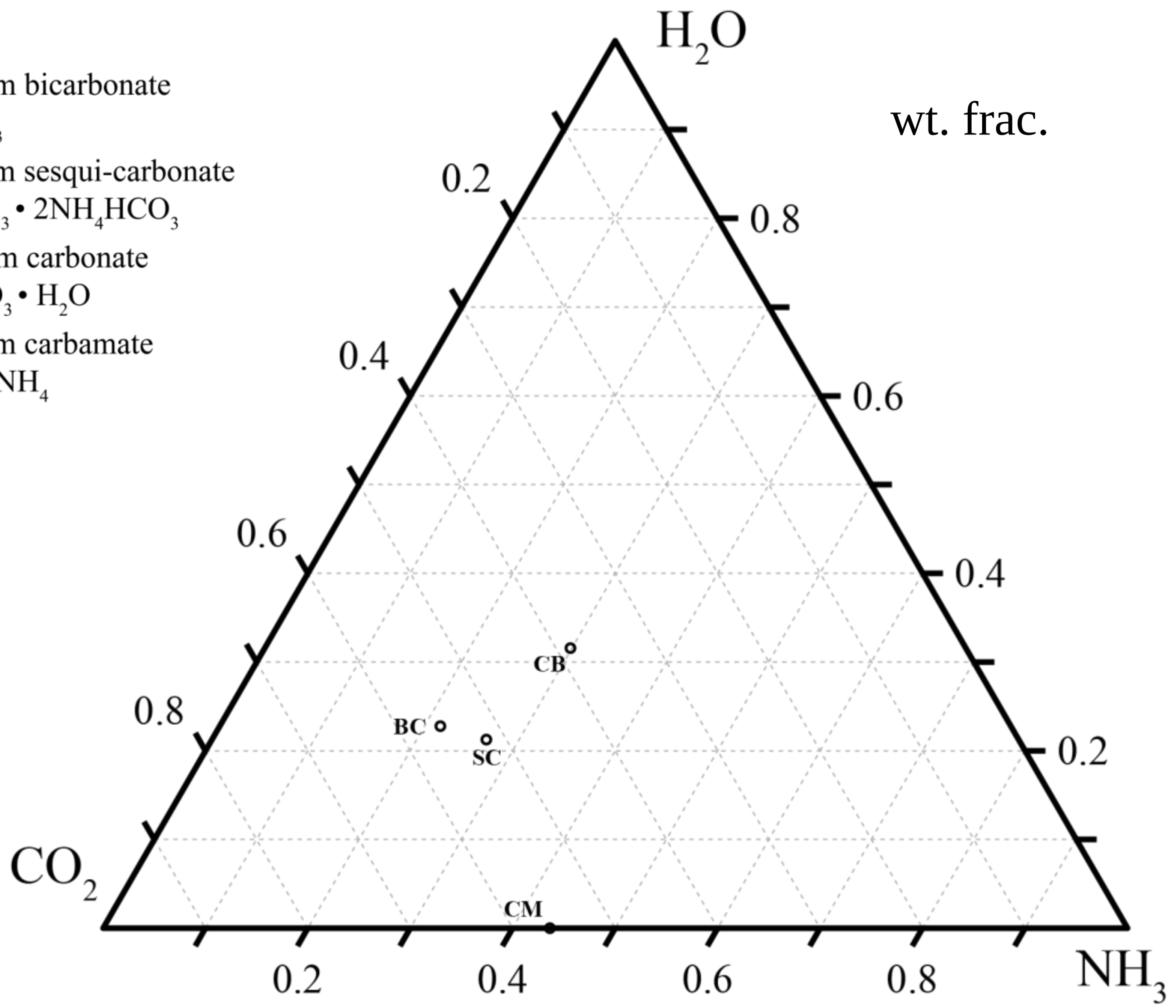




adapted from:
Darde et al., *Ind Eng Chem Res* 49 (2010) 12663-74

Phase diagram construction

- **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



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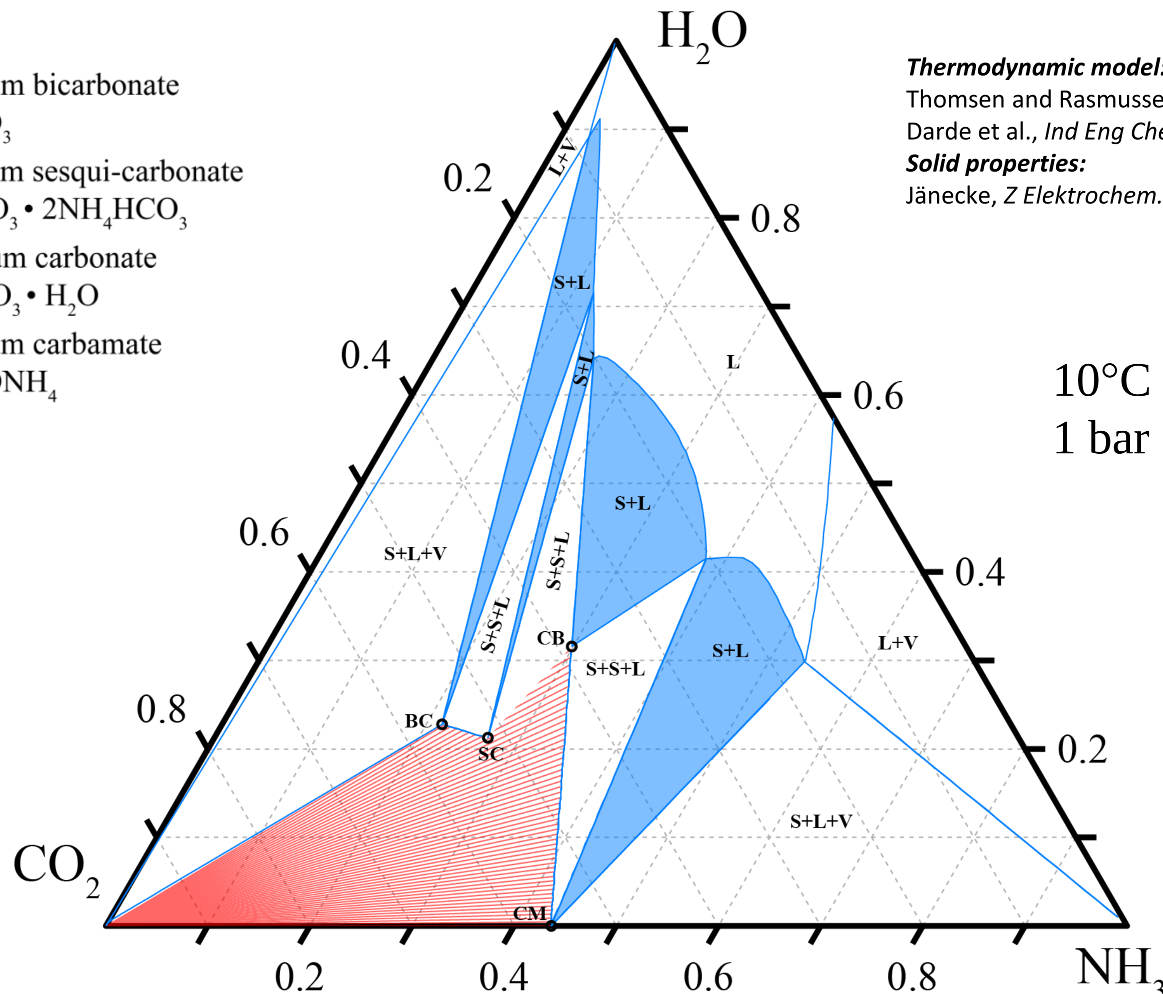

Thermodynamic model:
Thomsen and Rasmussen. *Chem Eng Sci.* 54 (1999)1787-1802
Darde et al., *Ind Eng Chem Res.* 49 (2010) 12663-74
Solid properties:
Jänecke, *Z Elektrochem.* 35 (1929) 9:716-28

10°C
1 bar

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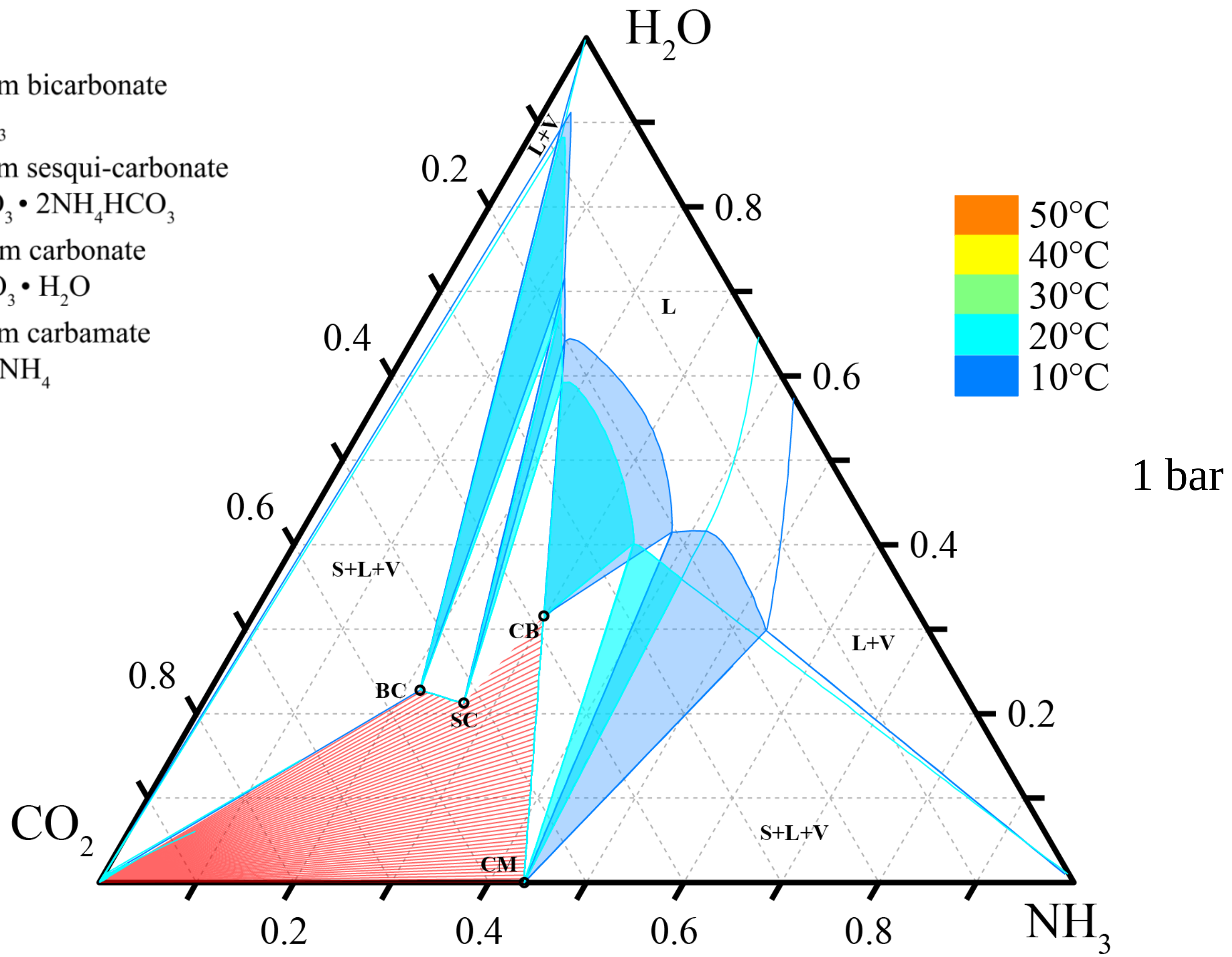

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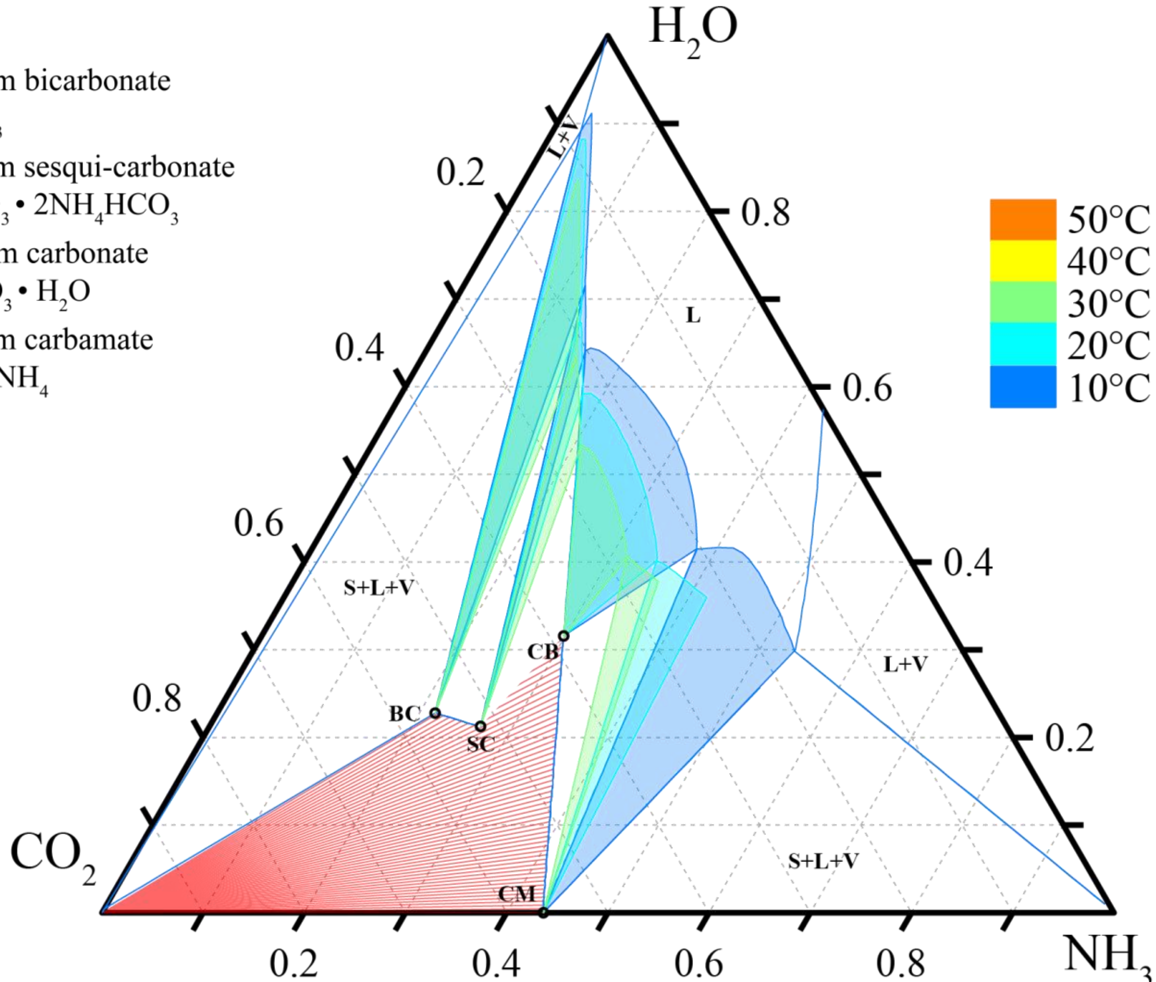

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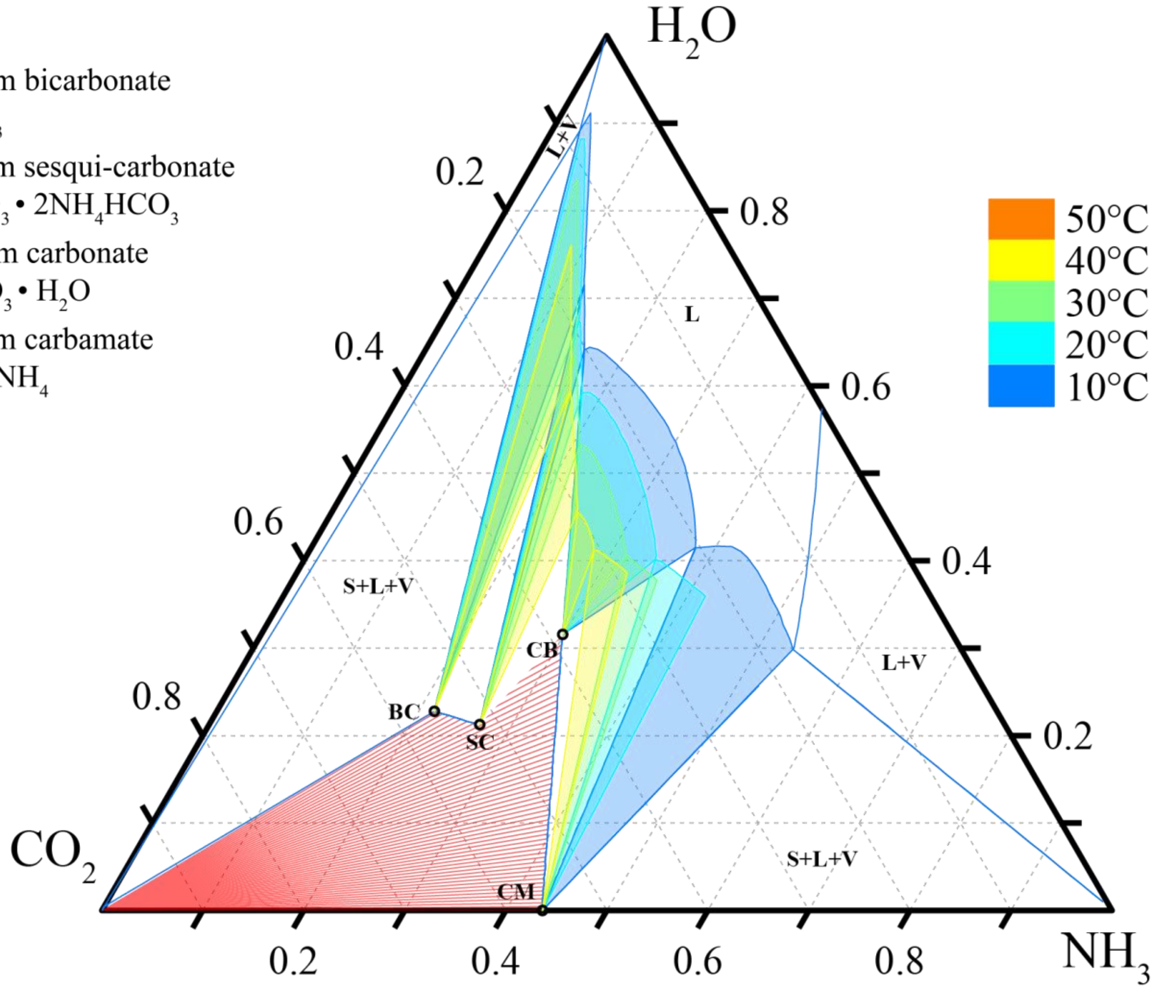

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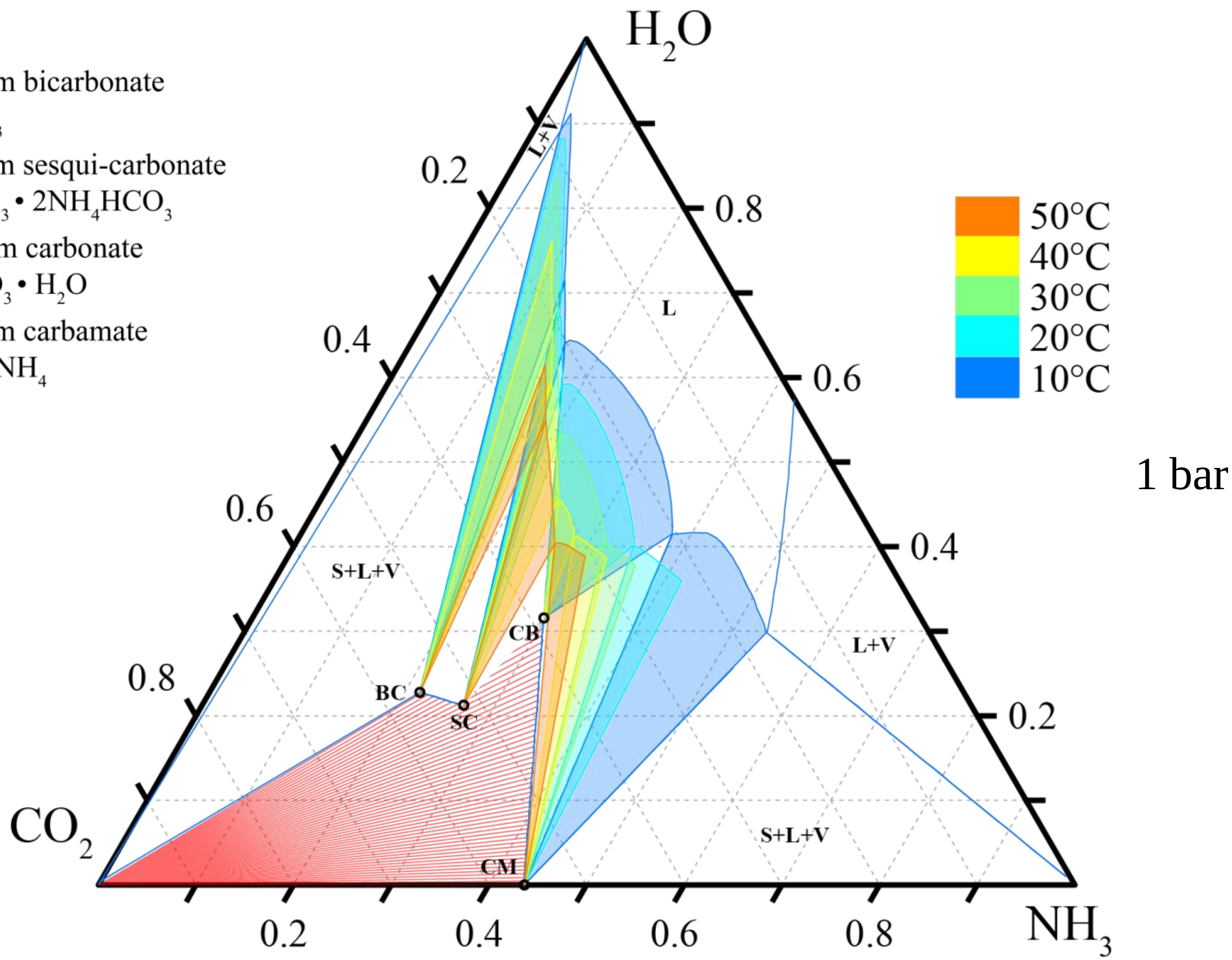

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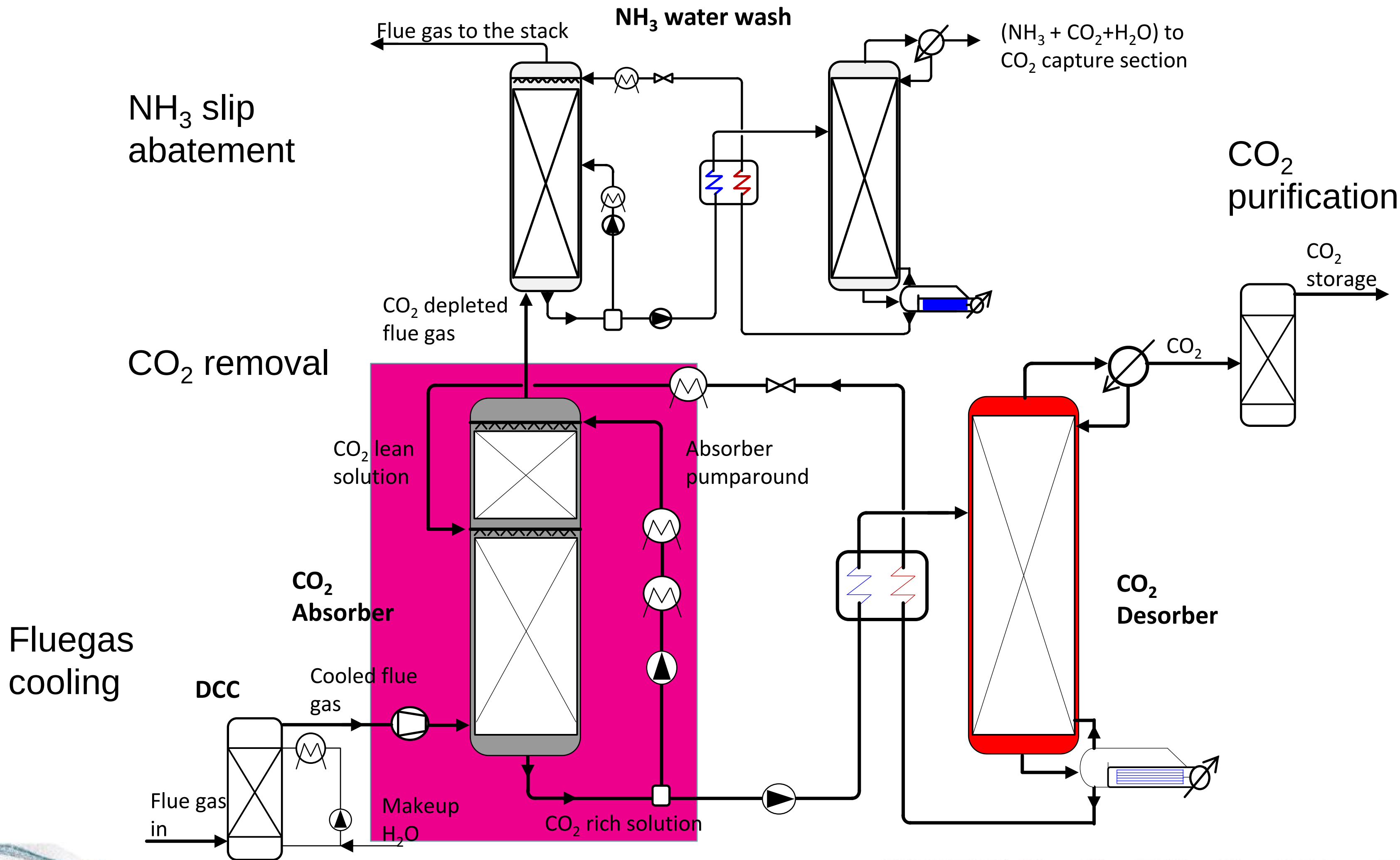
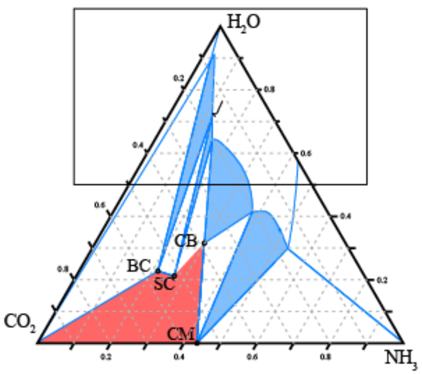
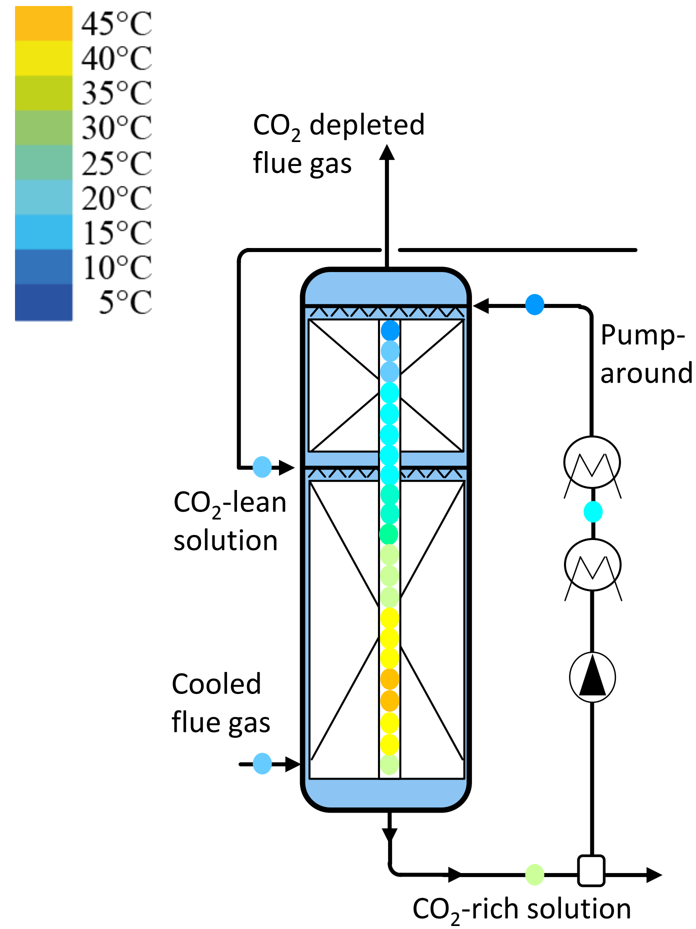
The Chilled Ammonia Process



CO_2 absorber





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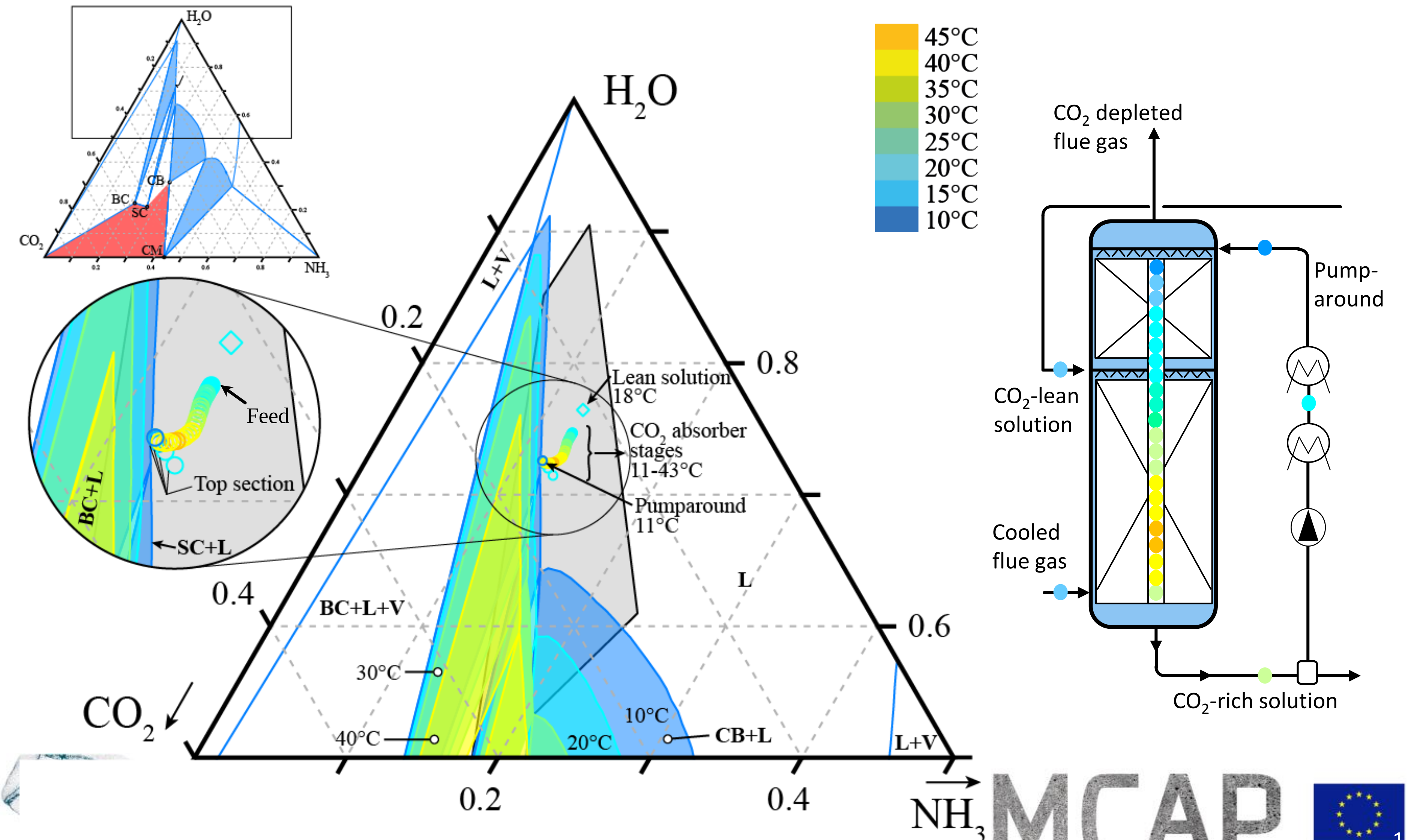

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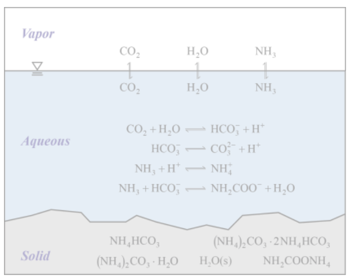

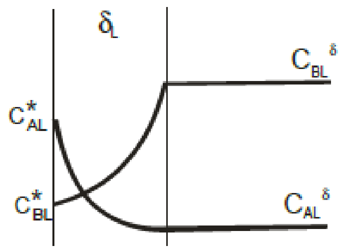

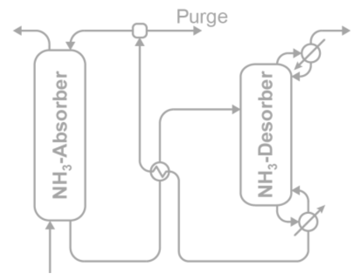

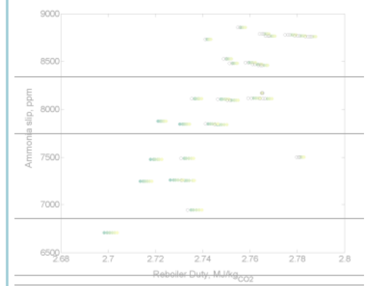

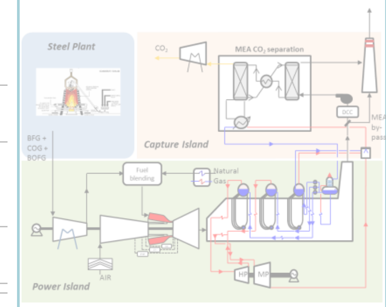

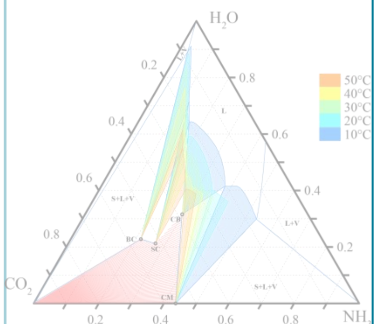

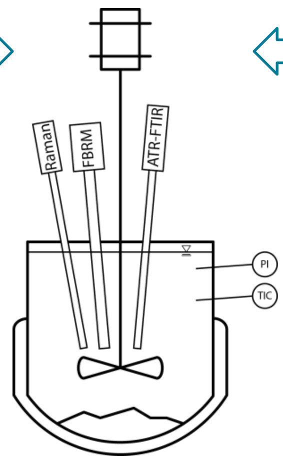

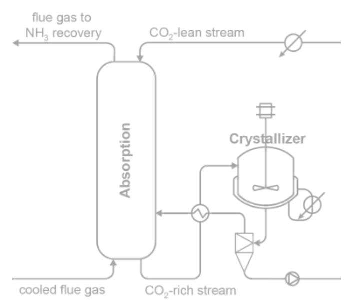

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Kinetics – equilibrium and rate-controlled reactions

Equilibrium reactions

(1) Self-ionization of water $$H_2O \overset{K_1}{\Leftrightarrow} OH^- + H^+$$

(2) Dissociation of bicarbonate $$HCO_3^- \overset{K_2}{\Leftrightarrow} CO_3^{2-} + H^+$$

(3) Protonation of ammonia $$NH_3 + H_2O \overset{K_3}{\Leftrightarrow} NH_4^+ + OH^-$$

Diffusion and rate controlled reactions

(4) Bicarbonate ion formation $$CO_2 + OH^- \overset{k_4, k_{-4}, K_4}{\Longleftrightarrow} HCO_3^-$$

(5) Carbamate ion formation $$CO_2 + NH_3 \overset{k_5, k_{-5}, K_5}{\Longleftrightarrow} NH_2COO^- + H^+$$

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Kinetics – chemical reaction mechanisms

Bicarbonate ion formation		
carbonic acid dissociation	$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+$	negligible contribution for pH>8 [4]
reaction with hydroxide ion	$CO_2 + OH^- \Leftrightarrow HCO_3^-$	
Carbamate ion formation		
Zwitterion mechanism[5,6]		
Zwitterion formation	$CO_2 + NH_3 \Leftrightarrow NH_3^+COO^-$	
deprotonation	$NH_3^+COO^- + B \Leftrightarrow NH_2COO^- + BH^+$	often considered non-rate-limiting[1-3]
Termolecular mechanism[7,8]	$CO_2 + NH_3 + B \Leftrightarrow NH_2COO^- + B$	
Elementary reactions mechanism[9]	$CO_2 + NH_3 \Leftrightarrow NH_2COO^- + H^+$	

[1] Pinsent et al. *Trans Faraday Soc.* 52 (1956) 1594-1598.
[2] Pinsent et al. *Trans Faraday Soc.* 52 (1956) 1512-1520.
[3] Puxty et al. *Chem Eng Sci.* 65 (2009) 915-922.
[4] Blauwhoff et al., *Chem Eng Sci.* 39 (1984) 207-225.
[5] Caplow. *J Am Chem Soc*. 90 (1968) 6795-6803.
[6] Danckwerts. *Chem Eng Sci.* 34 (1979) 443-446.
[7] Crooks and Donellan. *J Chem Soc Perkin Trans II.* 4 (1989) 331.
[8] da Silva and Svendsen. *Ind Eng Chem Res*. 43 (2004) 3413-3418.
[9] Wang et al. *J Phys Chem*. 115 (2011) 6405-6412.

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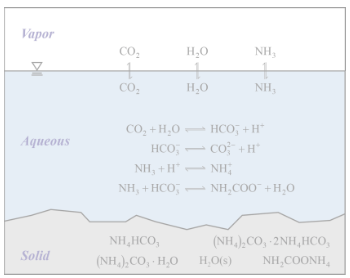

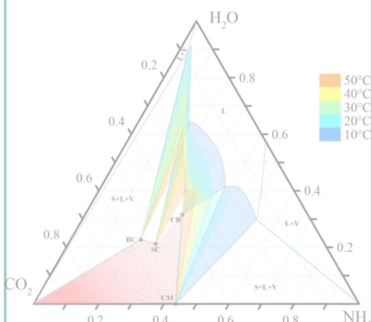

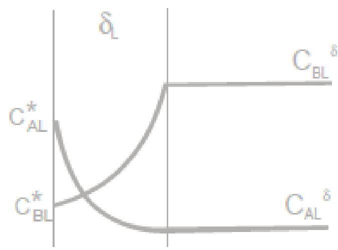

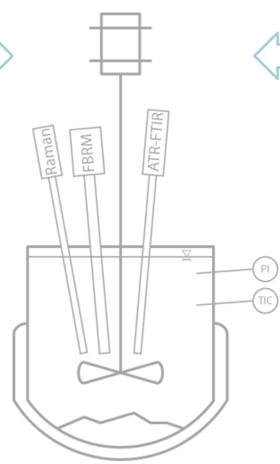

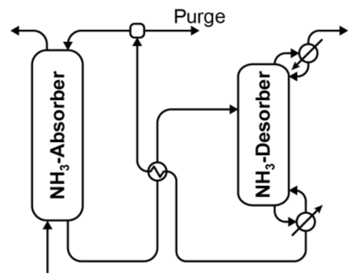

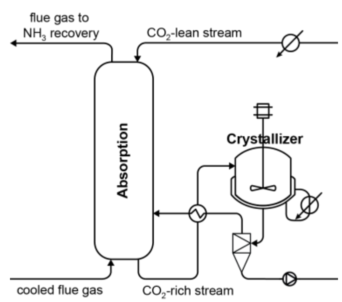

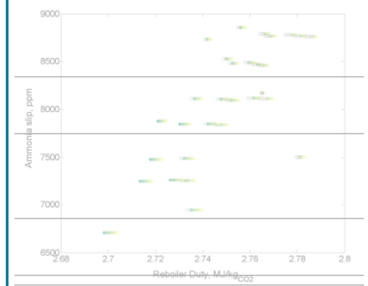

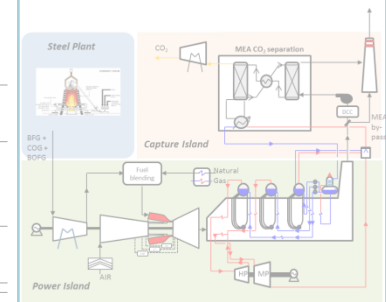

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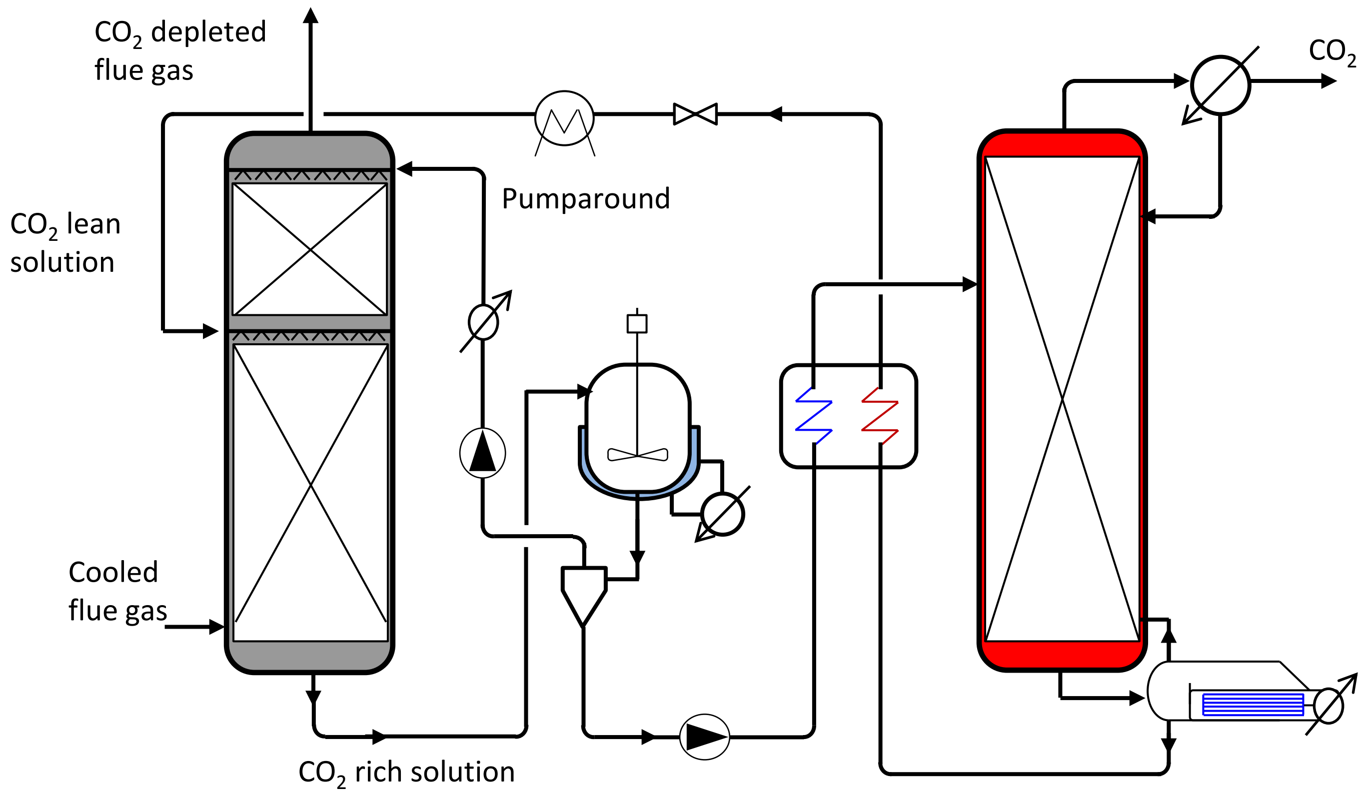
The chilled ammonia process with solid formation

Integrate solid formation into a next generation CAP

- Solid formation in the **crystallizer**
- **No solids in the columns**



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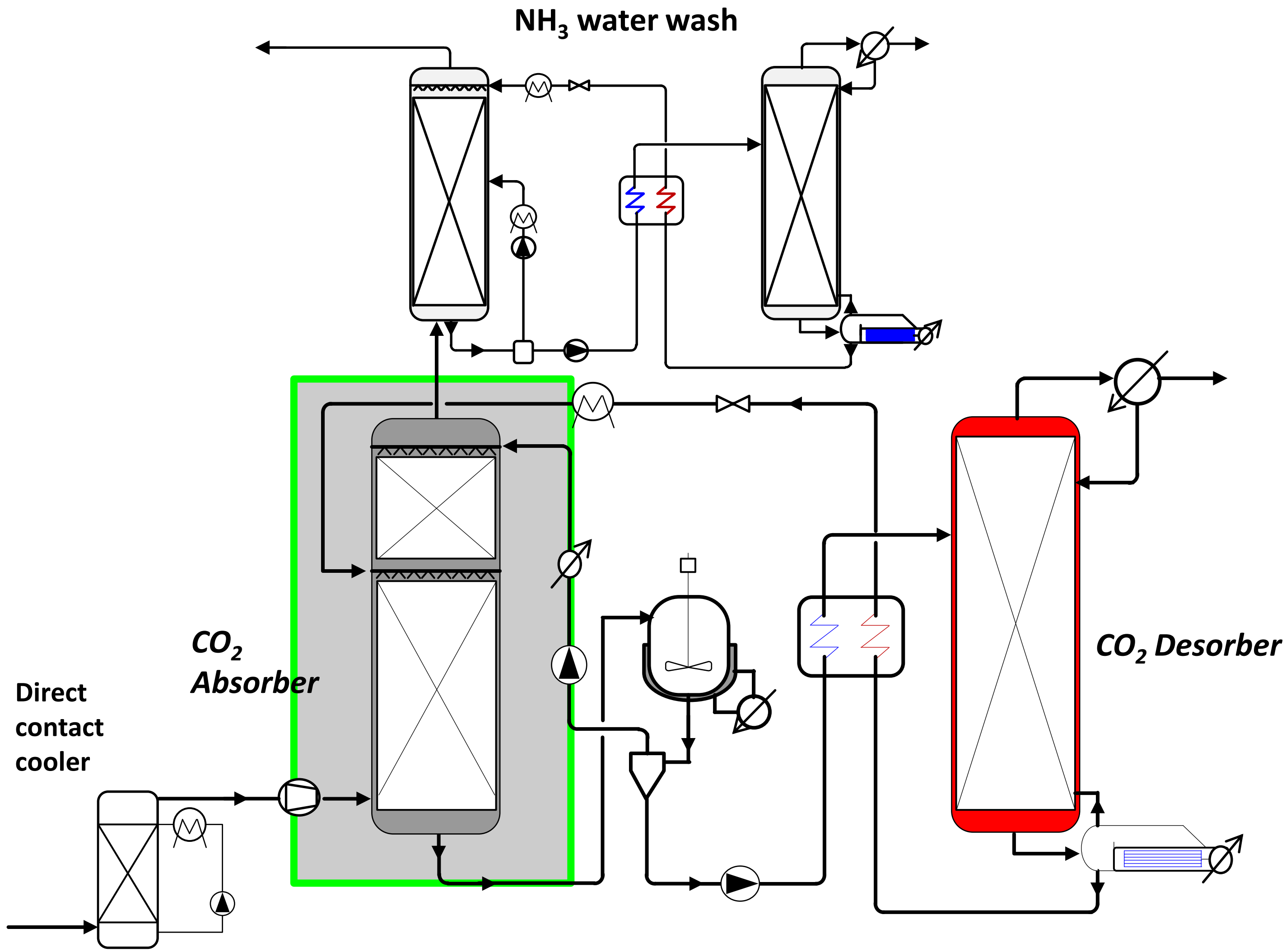
The chilled ammonia process with solids formation



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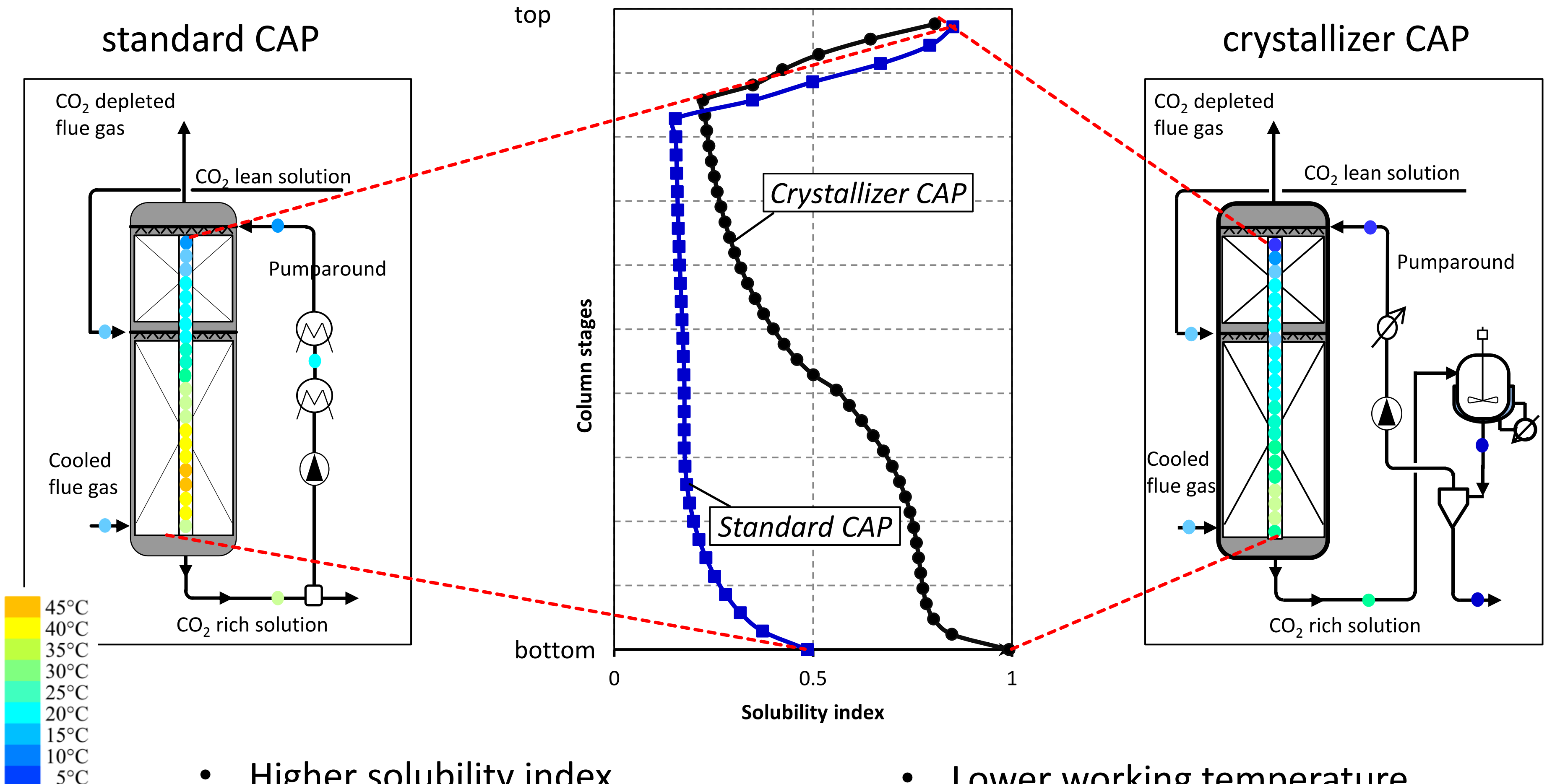
Absorber profile: standard vs crystallizer CAP



- Higher solubility index
- Higher CO_2 loading (lower flow rate)
- Lower working temperature
- Better ammonia slip control

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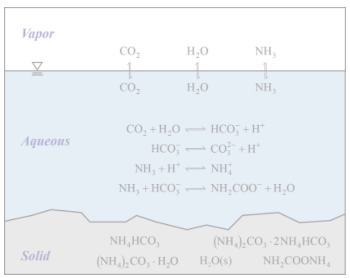
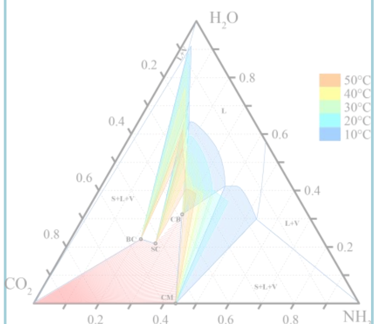
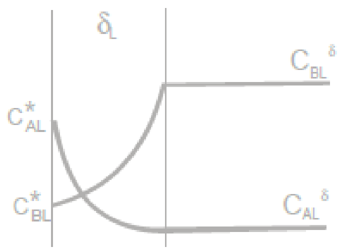
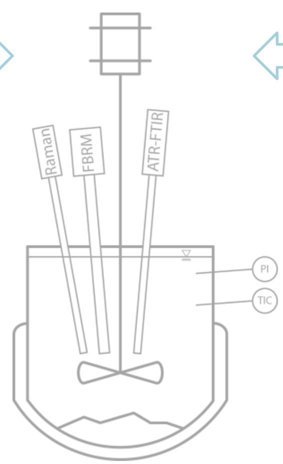
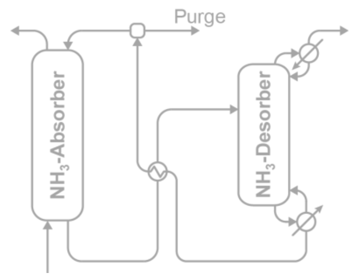
Thermo-dynamics	Kinetics	Process Synthesis	Process Optimization	Process Integration

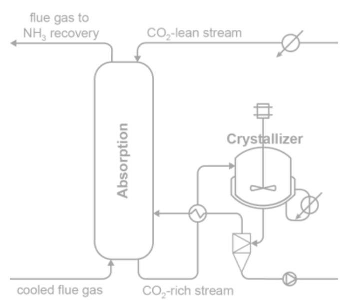


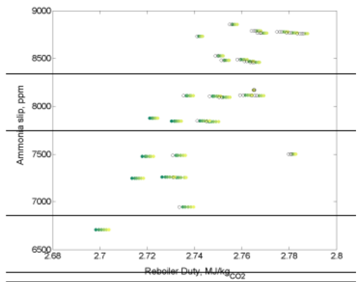


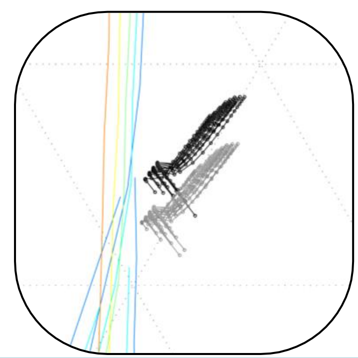


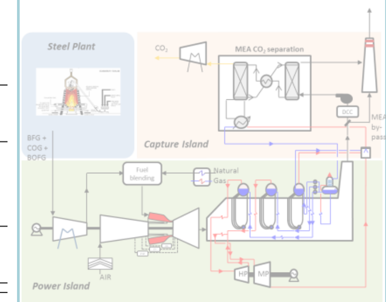












Total heat input, MW_{LHV}	576.8
POWER PRODUCTION	
Gas turbine*, MW_{el}	204.1
Steam turbine, MW_{el}	62.4
CONSUMPTIONS	
Steam cycle pumps, MW_{el}	1.5
CO2 compressor, MWel	17.5
MEA auxiliaries, MWel	7.4
Balance of Plant, MW_{el}	0.2
BALANCE	
Net Power Output, MW_{el}	240.1
Net Electric Efficiency, $\%_{LHV}$	**41.62**
CO_2 specific emissions, g/kWh_{el}	293.0
Avoided CO_2, %	**65.6**
SPECCA, MJ_{LHV}/kg_{CO2}	**3.76**

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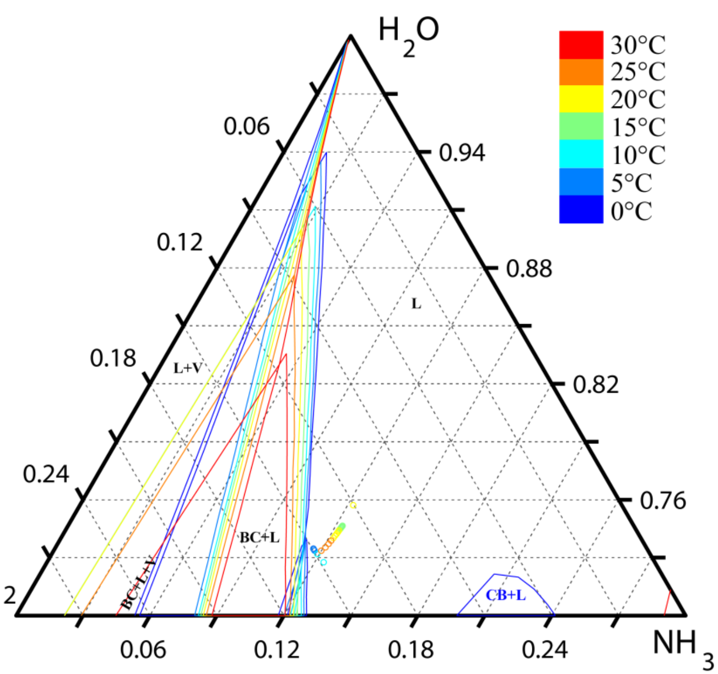
Definition of the CAP operating conditions

Process optimization

First Stage

Exploit the user sensitivity and knowledge of the process by visualizing the conditions on a CO_2-NH_3-H_2O ternary phase diagram



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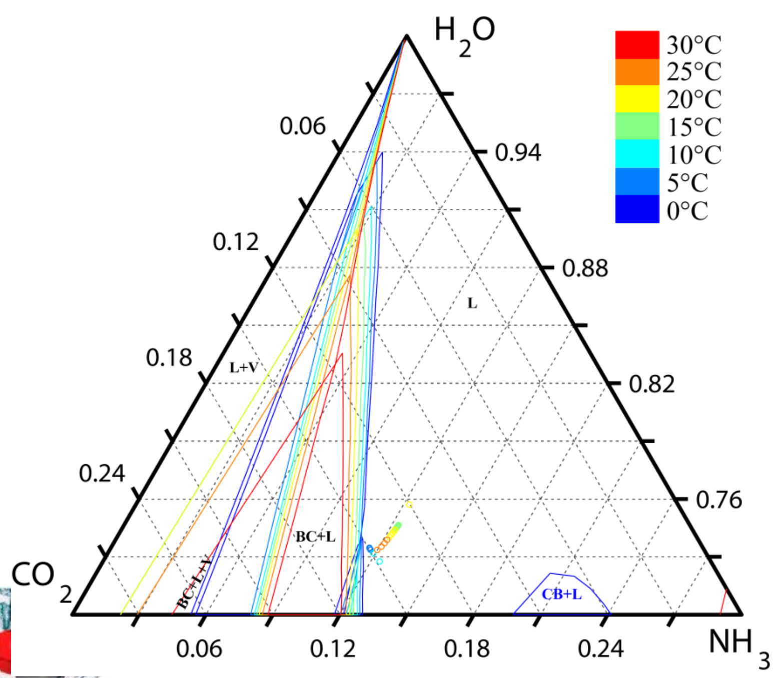
Definition of the CAP operating conditions

Process optimization

First Stage

Exploit the user sensitivity and knowledge of the process by visualizing the conditions on a CO_2-NH_3-H_2O ternary phase diagram



Second Stage

Optimization of the CAP in a limited feasible region of the operating variables

MATLAB overarching structure

Sensitivity analysis - CO_2 capture section

Input parameters:
- NH_3 fraction in water
- CO_2 loading lean stream
- Absorber loading
- L/G
- Reboiler Duty

Matlab+Aspen

Rigorous optimization - NH_3 removal section

Minimized function:
- Specific reboiler duty

Input variables:
- L/G
- Reboiler duty

Constraints:
- NH_3 removal
- CO_2 capture

Aspen

Final operating conditions

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ECRA-Cemcap Workshop

Criticalities for CAP application to cement plant conditions

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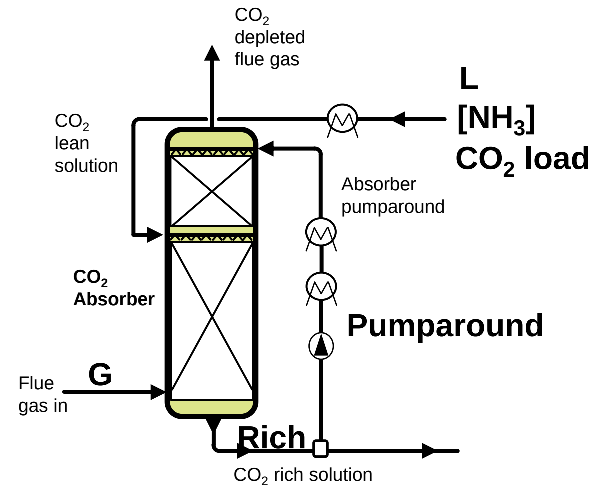
Outline



- Increment in the content of CO_2 in the flue gas
  - Power plant 2 – 16%mol
  - Cement plant up to 30%mol
- Modifications of absorber conditions

To reach 90% of CO_2 recovery in the flue gas from the cement plant:
(i) Increase the liquid-to-vapor flowrate
(ii) Increase the ammonia content in the CO_2-lean stream and/or
(iii) Decrease the CO_2 loading of the CO_2-lean solution

→

Multiple combinations:
(i) L/G
(ii) Pumparound/Rich
(iii) $[NH_3]_{CO2\text{-}lean}$
(iv) $(CO_2\ load)_{CO2\text{-}lean}$

- Cement-like CO_2 content leads to different operating conditions of CAP and/or process modifications

Absorber simulations – Exemplary cases

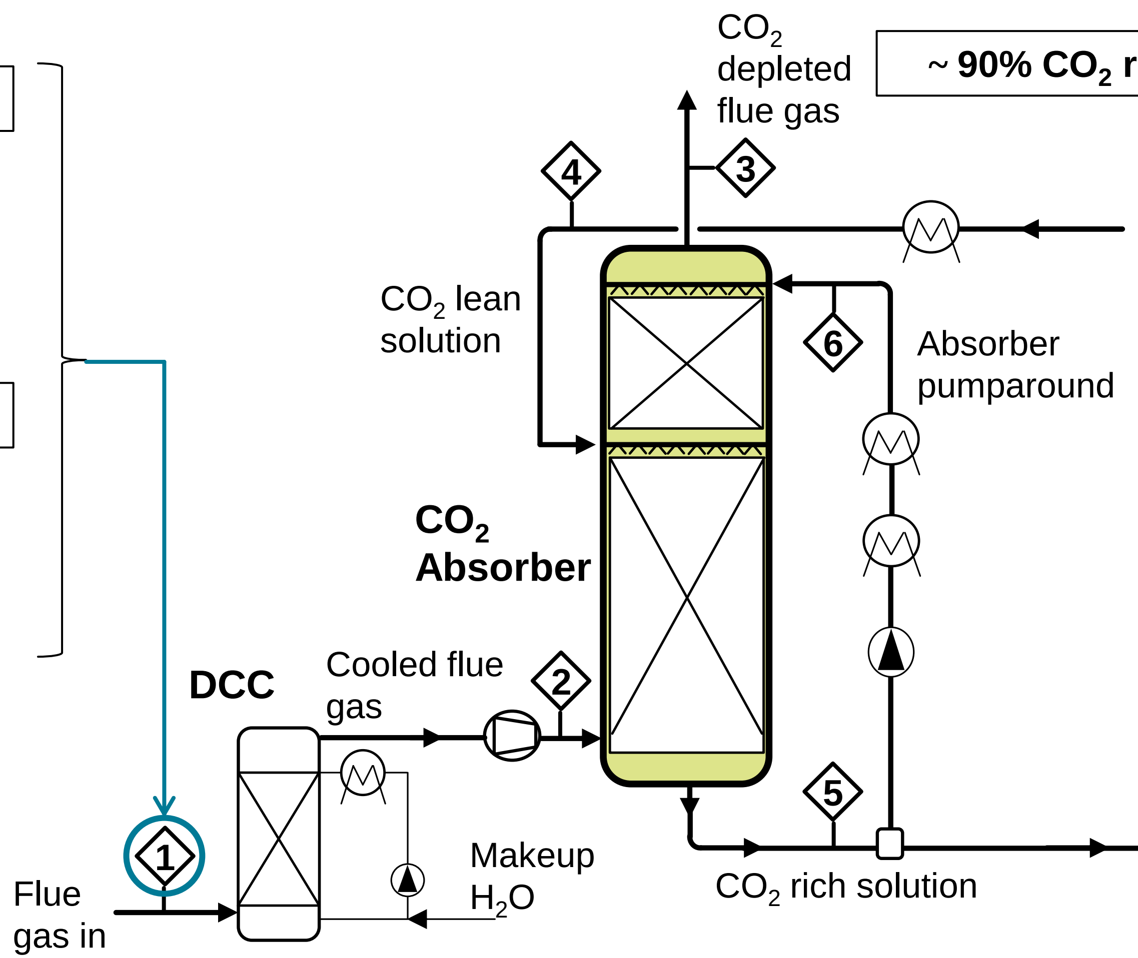
Power Plant – Base case

y_{air} = 0.84
y_{CO2} = 0.16
y_{H2O} = 0
T = 140°C

Cement Plant cases

y_{air} = 0.70
y_{CO2} = 0.30
y_{H2O} = 0
T = 110°C

~ 90% CO_2 recovery



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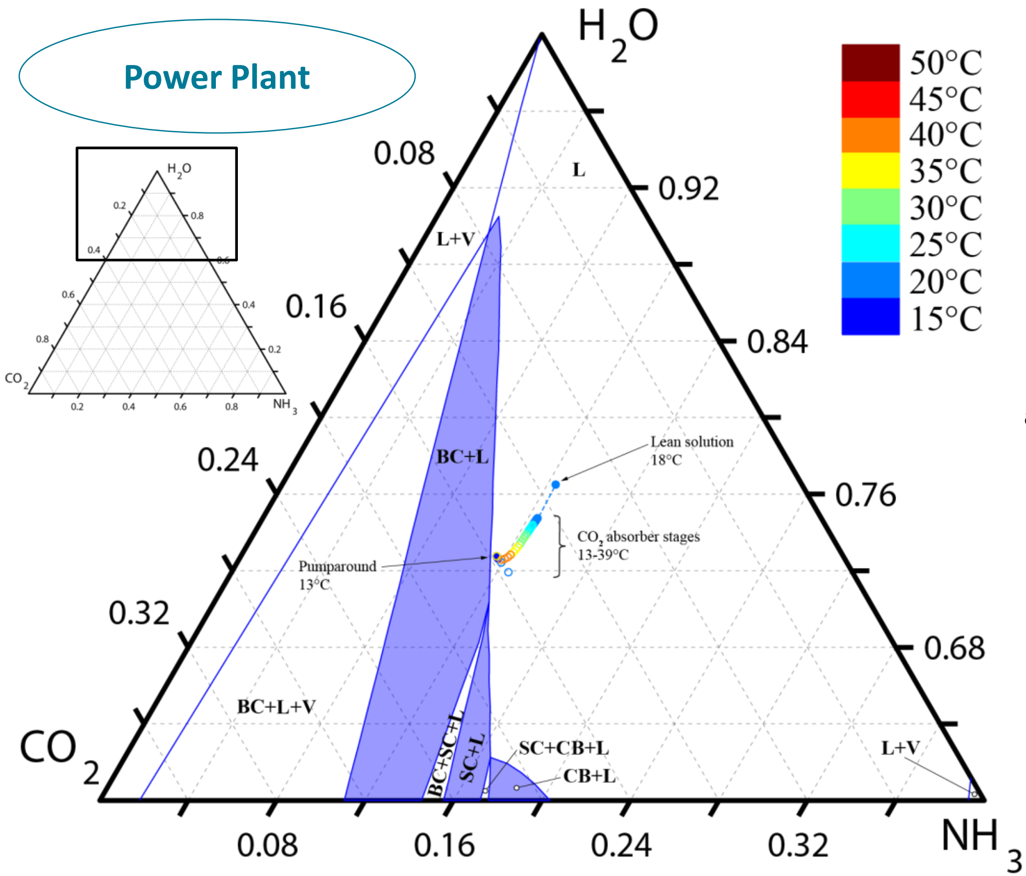
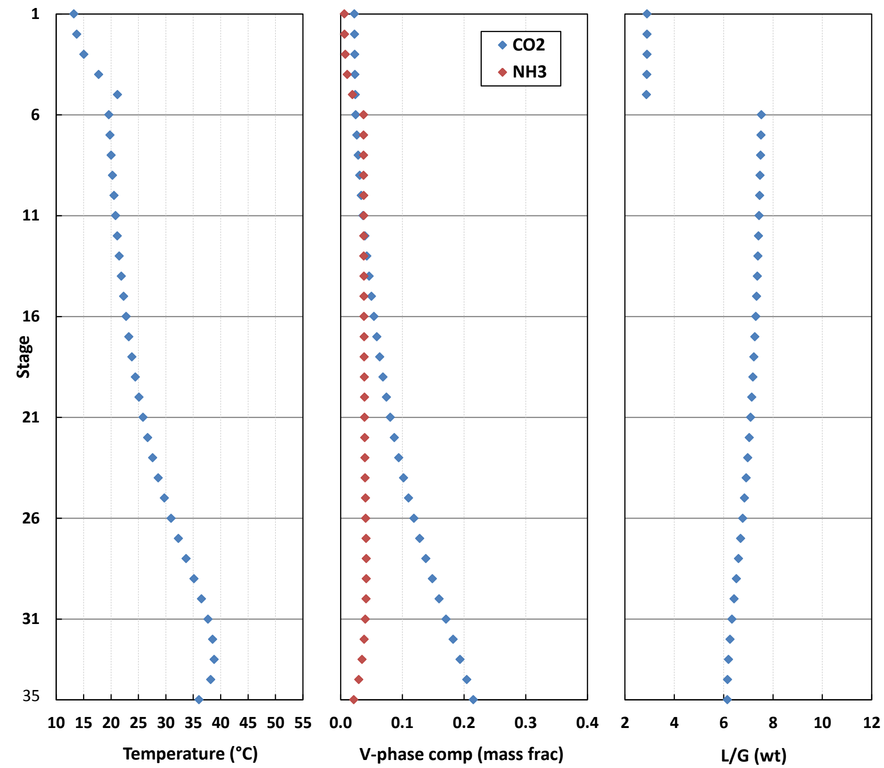
Absorber simulations – Exemplary cases

Power Plant





Inlet flue gas	$y_{CO2} = 0.16$
CO_2-lean stream	CO_2load = 0.35 mol_{CO2}/mol_{NH3}
	$[NH_3]$ = 14 %wt (binary)
Absorption process	L/G = 3.7 kg/kg
	Pumparound/Rich = 0.36
	CO_2 capture ≈ 90 %
	NH_3 slip ≈ 10000 ppm_v

Two differenciated regions in the absorber separated by the CO_2-lean stream:

(i) NH_3-uptake

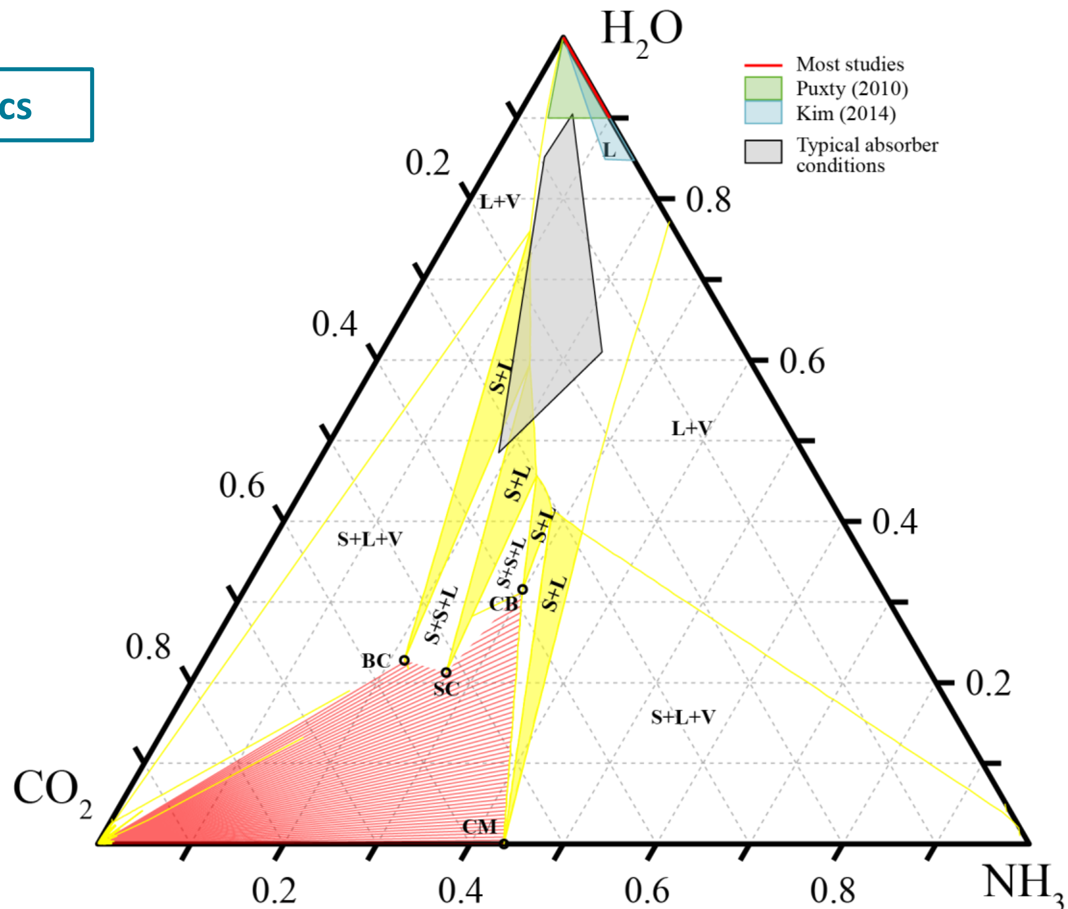
(ii) CO_2-uptake

Modelling

Thermodynamic model

Simplified kinetics

Power Plant



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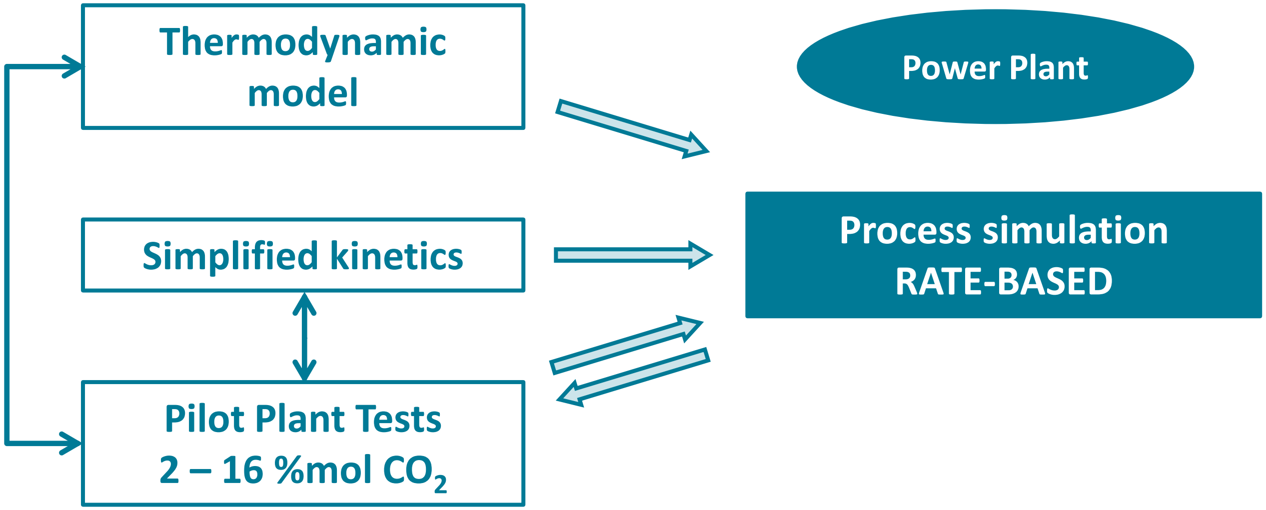
Modelling


Thermodynamic model
Simplified kinetics
Pilot Plant Tests
2 – 16 %mol CO_2
Power Plant
Process simulation
RATE-BASED

Modelling

Power Plant

Process simulation
RATE-BASED

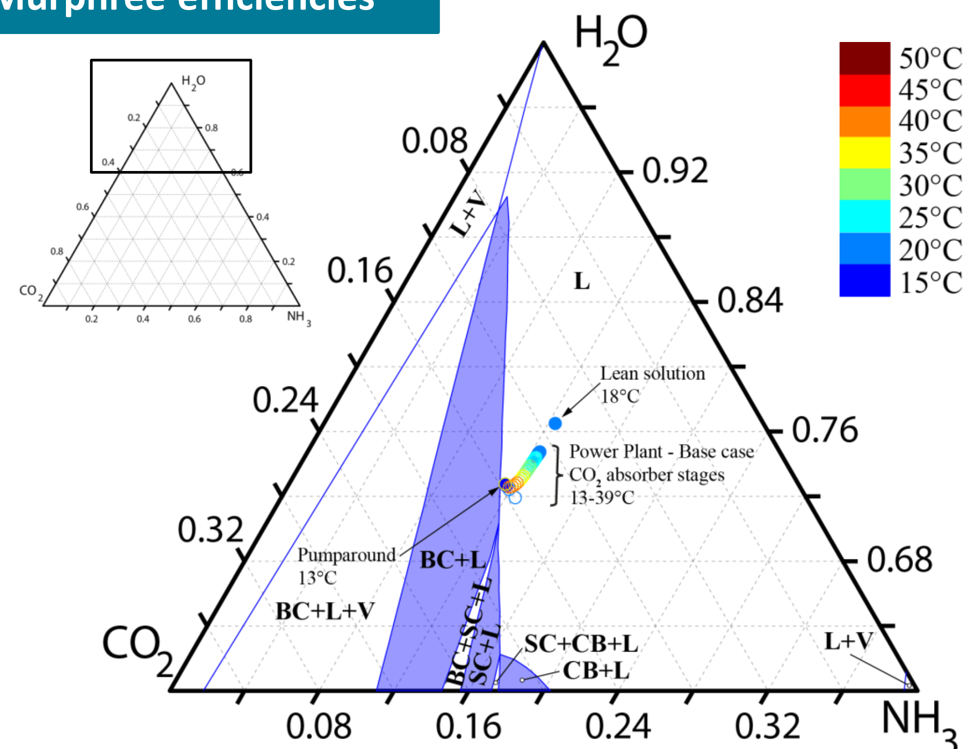
→ Murphree efficiencies →

Power Plant

Process simulation
EQUILIBRIUM-BASED
Murphree efficiencies

→

Process Integration



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Modelling

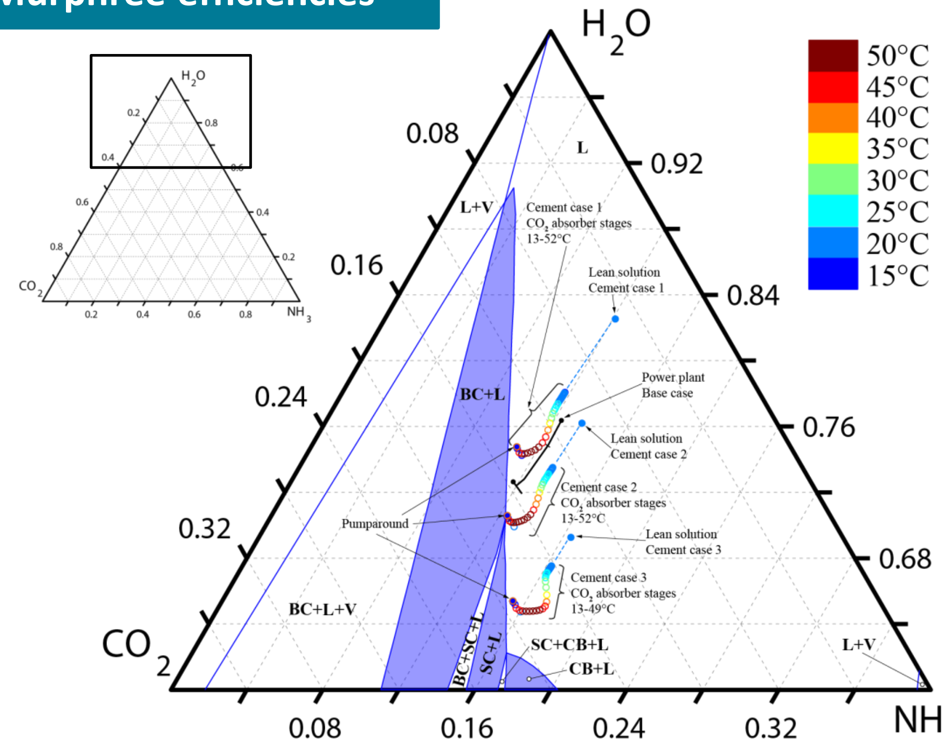
Power Plant

Cement Plant

Process simulation
RATE-BASED

Murphree efficiencies

Process simulation
EQUILIBRIUM-BASED
Murphree efficiencies



Modelling

Thermodynamic model

Simplified kinetics

Pilot Plant Tests
2 – 16 %mol CO_2

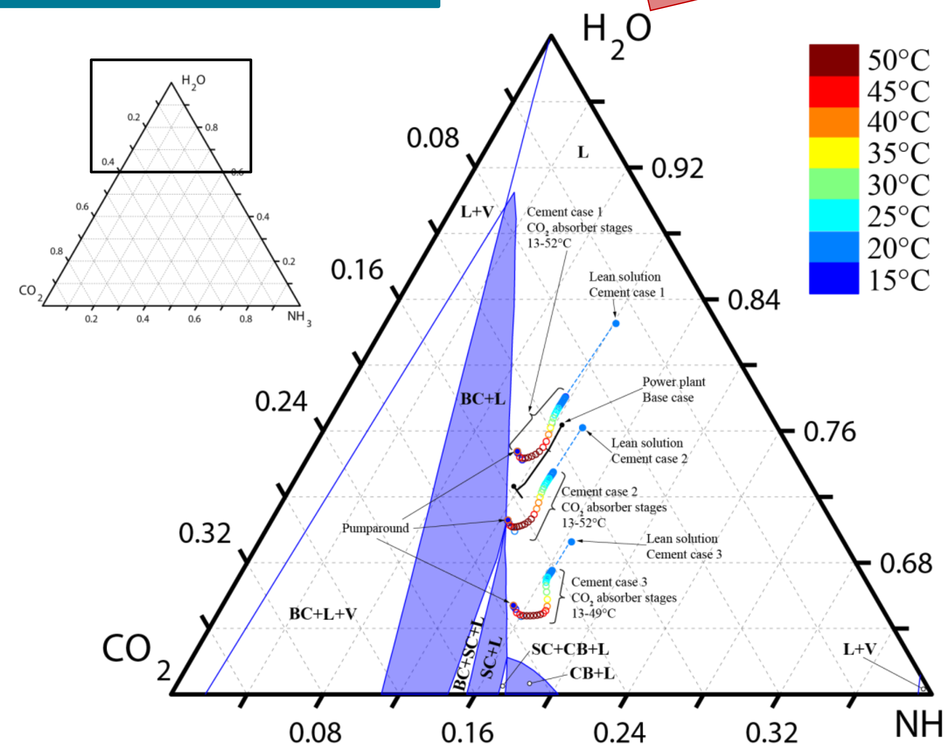
Power Plant

Cement Plant

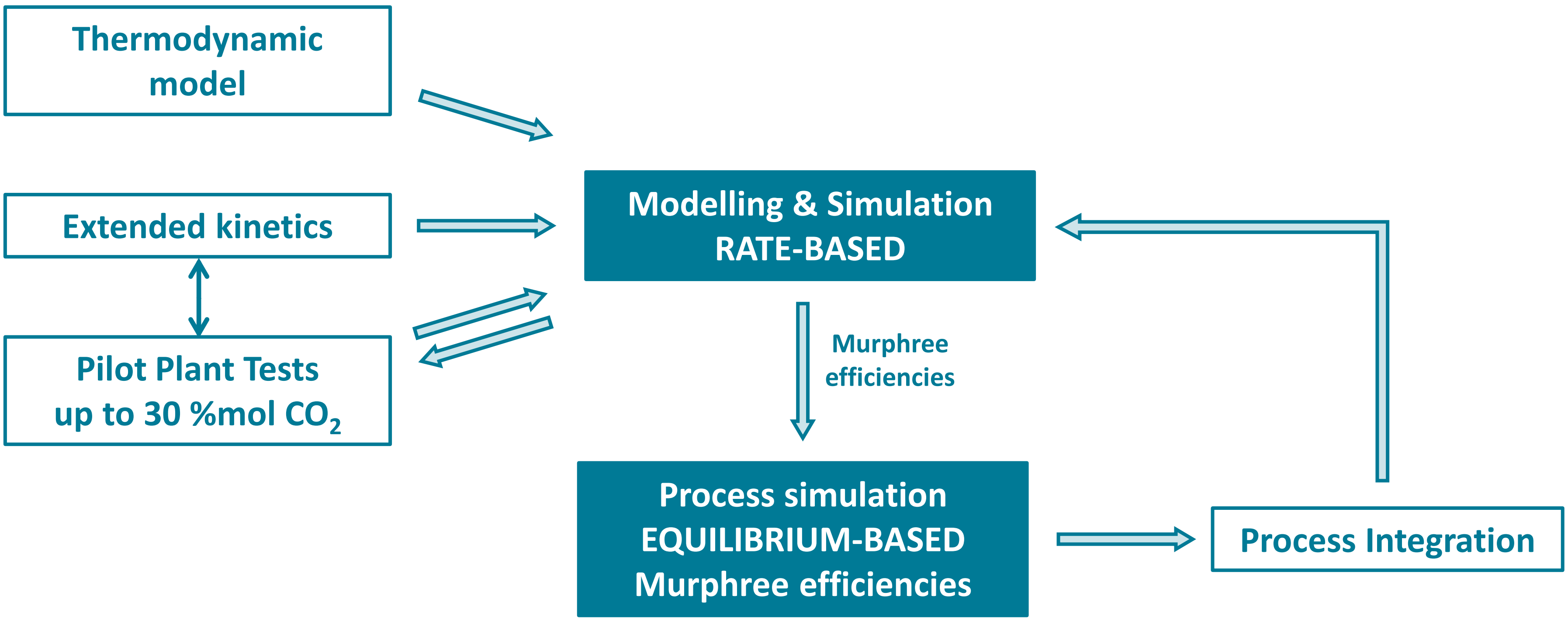
Process simulation
RATE-BASED

Murphree efficiencies???

~~**Process Integration**~~



CEMCAP approach



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