ETH zürich

Application of a chilled ammonia-based process for CO_2 capture to cement plants

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GHGT-13, November 14-18, 2016

Talk outline

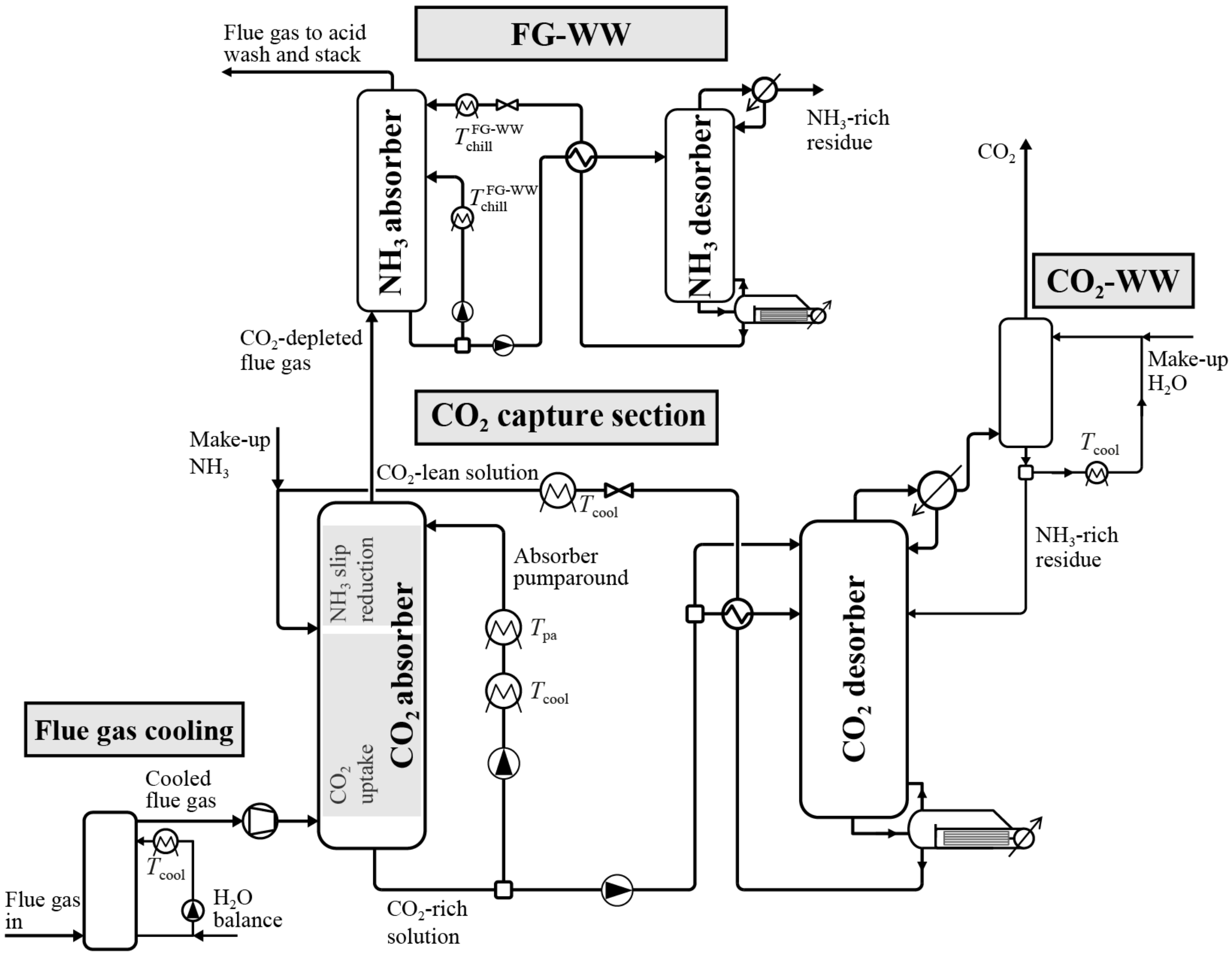
- **Introduction**
- **The Chilled Ammonia Process (CAP)**
- **Scope** of the study
- CAP **model** for simulations
- Heuristic **optimization** approach and results
- **Conclusions**

CO_2 emissions from cement & the CAP

- 5% of global antrophogenic CO_2 emissions
- ~ 0.58 t CO_2/t cement (BAT)
  - ~ 50 – 60% process-related emissions ➔ **CCS required**

- Why the Chilled Ammonia Process (CAP)?
  - Low thermal energy for regeneration required
    - Limited waste heat available in cement plants
  - Stable in the presence of impurities
  - Technology demonstrated in various facilities of different scale

The Chilled Ammonia Process



From power plants to cement plants

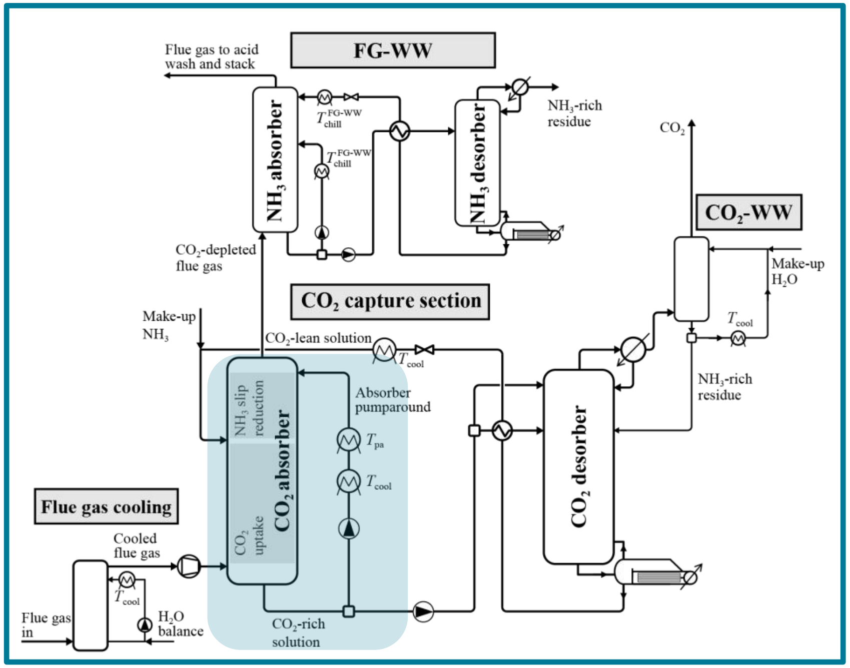
Model-based optimization

- Process complexity
- Thermodynamics
- Kinetics
- Heat integration

NG power plants and cracker
4 %vol. CO_2

Coal-fired power plants
14 %vol. CO_2

Cement plants
15 – 35%vol. CO_2

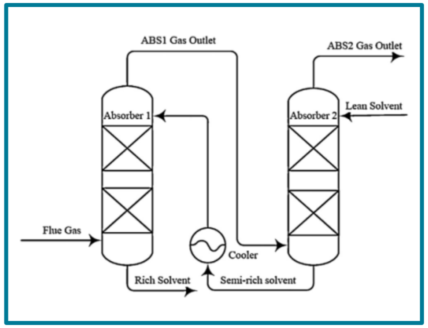


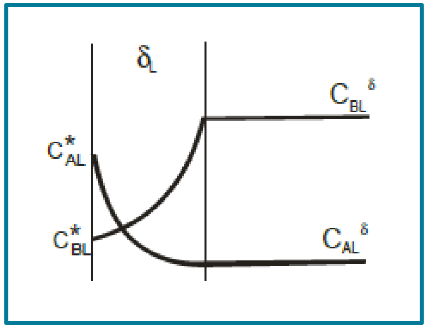
Adaptation of operating conditions

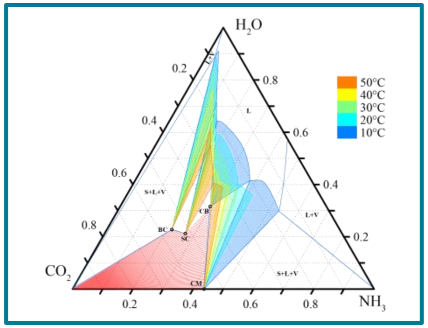
- Higher L/G
- Higher NH_3 content
- Lower CO_2 loading
- Combination

Scope of the study

Pilot plant tests CSIRO	Rate-based model (Aspen Plus)	Equilibrium-based model (Aspen Plus)





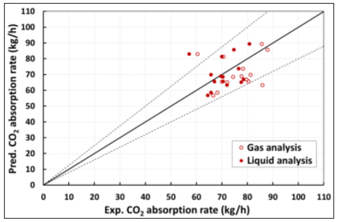


Starting point

0
- Thomsen thermodynamic model[1,2]
- Murphree effs. for power plants from literature[3,4]

This work

2 **Model validation**



1
- Literature research
- Adaptation of kinetic parameters

Computationally intensive

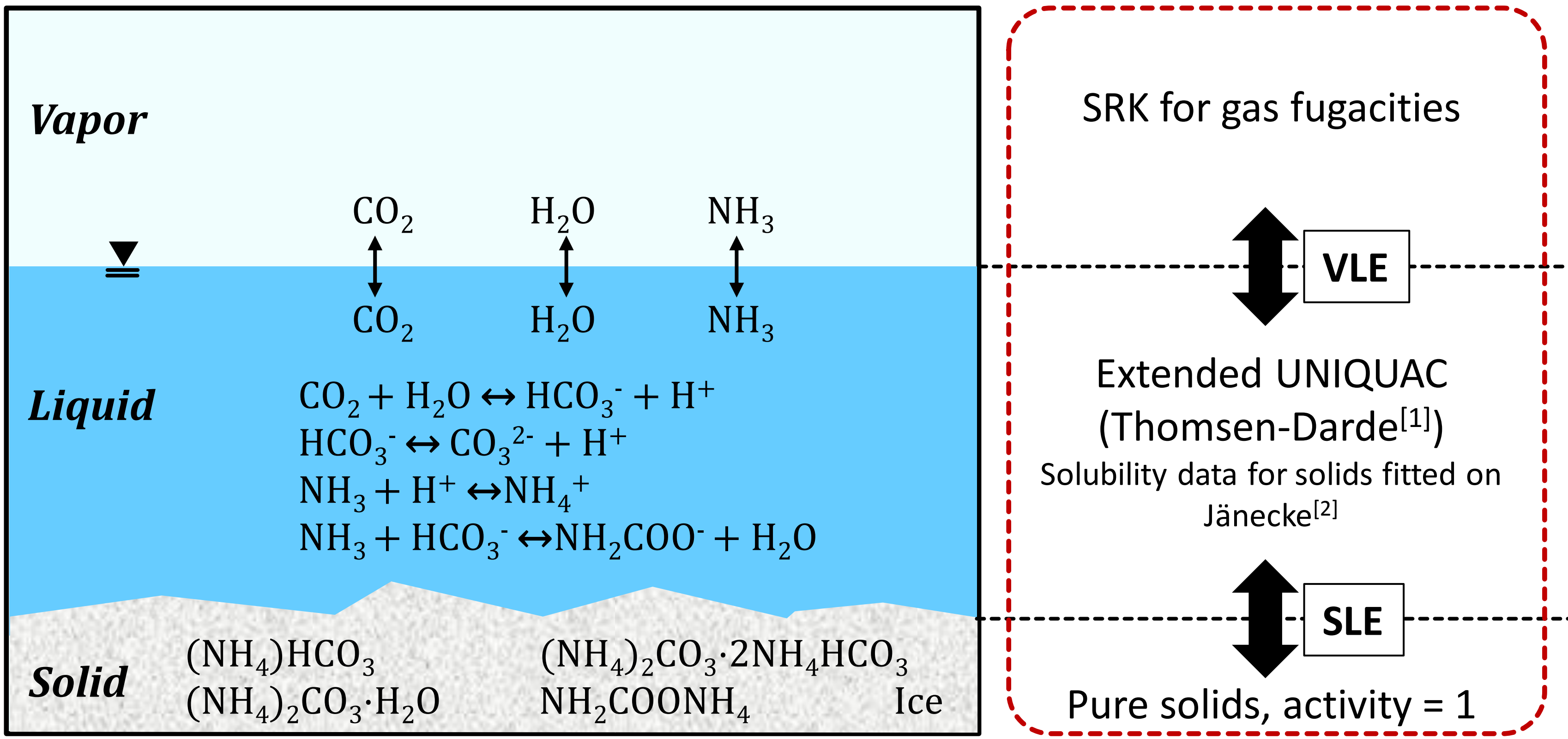
3
- Ad-hoc Murphree effs. for cement plants
- Thomsen thermodynamic model[1,2]

4 **Model-based optimization**

[1] Thomsen and Rasmussen *Chem Eng Sci* 54 (1999) 1787-1802
[2] Darde et al. *Ind Eng Chem Res* 49 (2010) 12663-74
[3] Sutter et al. *Faraday Discuss* 192 (2016) 59-83
[4] Jilvero et al. *Ind Eng Chem Res* 53 (2014) 6750-6758

Thermodynamic model: CO_2-NH_3-H_2O system

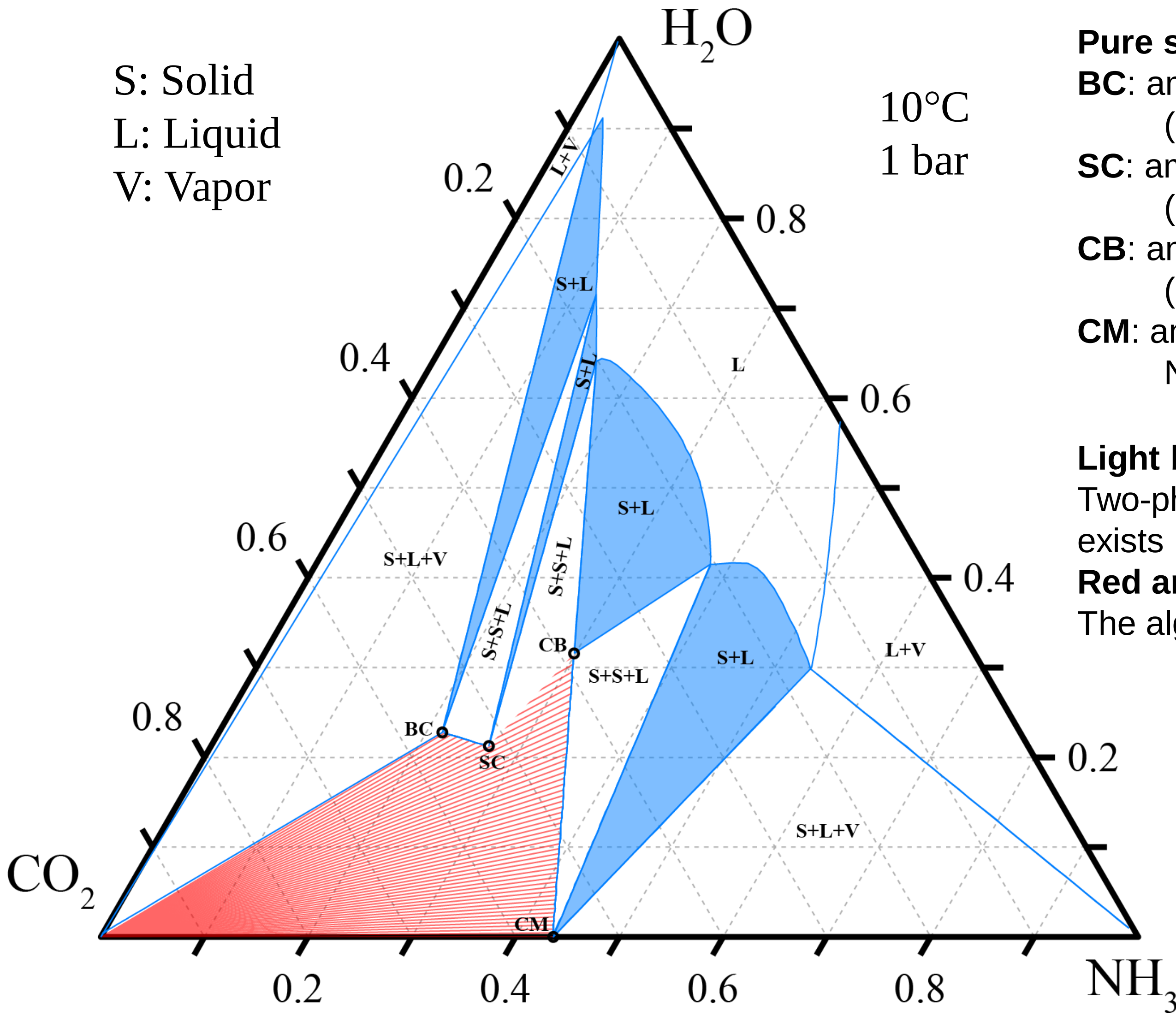
Thomsen model to predict the system thermodynamics



External routine in Aspen from Thomsen group

[1] Darde et al. *Ind Eng Chem Res* 49 (2010) 12663-74
[2] Jänecke *Z Elektrochem* 35 (1929) 9:716-28

Phase diagram: CO_2-NH_3-H_2O system



Pure solids

BC: ammonium bicarbonate
$(NH_4)HCO_3$

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

CB: ammonium carbonate
$(NH_4)_2CO_3{\cdot}H_2O$

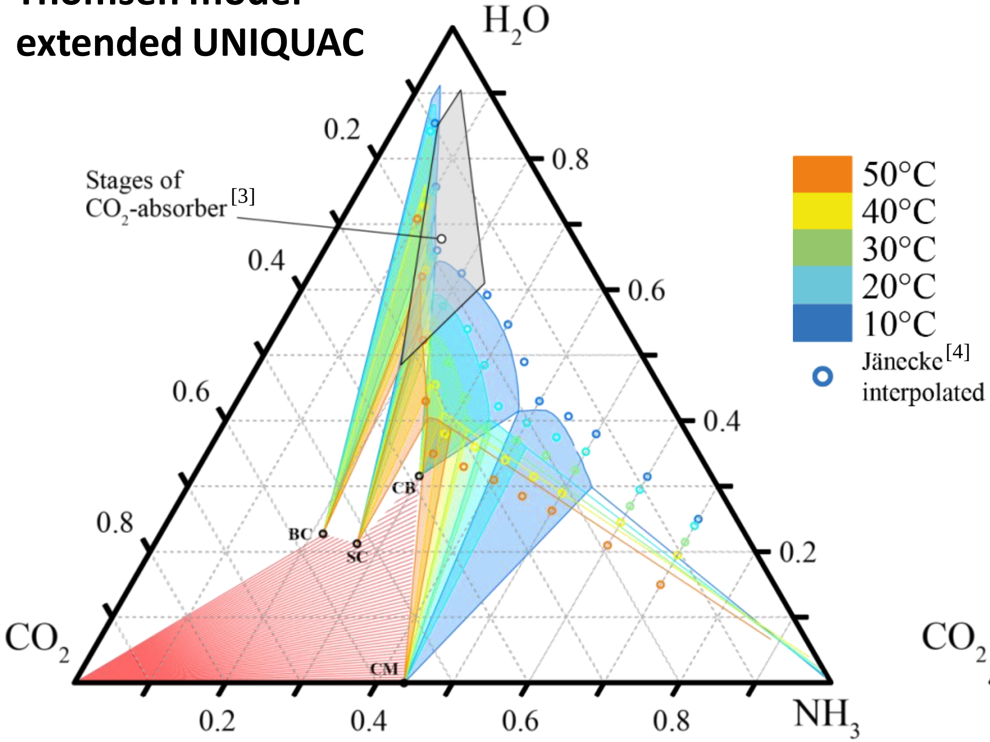
CM: ammonium carbamate
NH_2COONH_4

Light blue area:
Two-phase region where the solid exists in its mother liquor

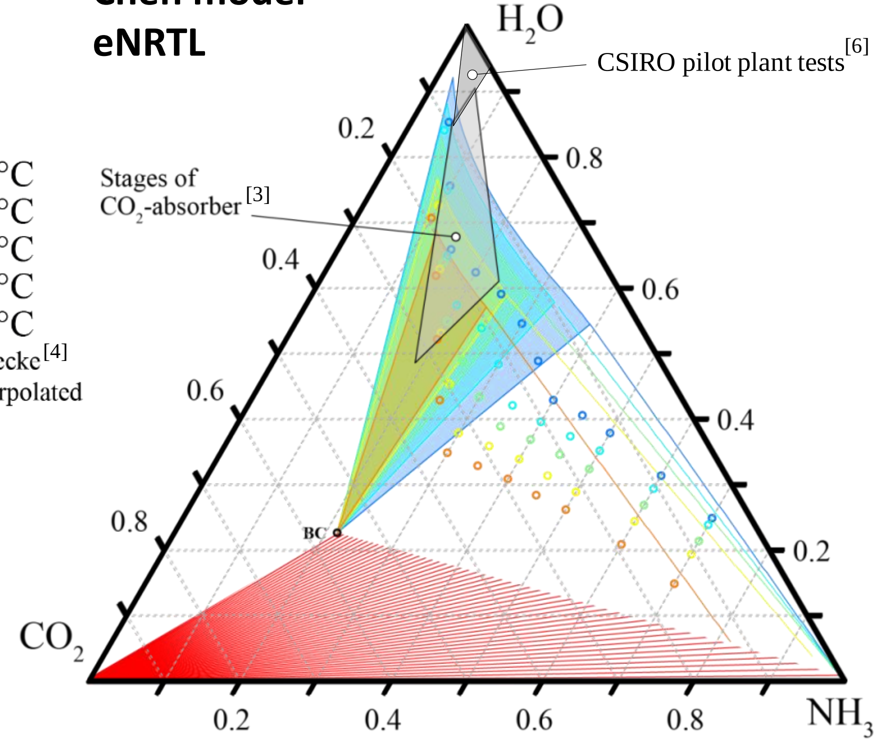
Red area:
The algorithm does not converge

Thermodynamic model: Comparison

Thomsen model[1,2]
extended UNIQUAC



Chen model[5]
eNRTL



Differences between the two models are even more pronounced if we consider the speciation in the liquid phase

[1] Thomsen and Rasmussen *Chem Eng Sci* 54 (1999) 1787-1802
[2] Darde et al. *Ind Eng Chem Res* 49 (2010) 12663-74
[3] Sutter et al. *Chem Eng Sci* 133 (2015) 170-180
[4] Jänecke *Z Elektrochem* 35 (1929) 9:716-728
[5] Que and Chen *Ind Eng Chem Res* 50 (2011) 11406-11421
[6] Yu et al. *Chem Eng Res Des* 89 (2011) 1204-1215

Rate-based model

Aspen Plus RadFrac distillation model (RateSep)

Simplifying: $$N_{CO_2} = K_{G,CO_2} V A_{int} (P_{CO_2} - P^*_{CO_2})$$

$$K_{G,CO_2} = f \begin{pmatrix} \text{physical mass transfer} \\ \text{reaction kinetics in the L} - \text{phase} \end{pmatrix}$$

$$A_{int} = f(\text{hydrodynamics})$$

} Correlations available in Aspen Plus

$$(P_{CO_2} - P^*_{CO_2}) = f(\text{thermodynamics})$$

Other works: In combination with Chen model[1]

This work:

Thomsen thermodynamic **model** to compute the **driving force** instead

[1] Qi et al. *Int J Greenh Gas Con* 17 (2013) 450-461

Rate-based model: Kinetics of speciation

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 $NH_3 + H_2O \overset{K_3}{\Leftrightarrow} NH_4^+ + OH^-$

Kinetic reactions

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

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

Pinsent kinetic models [1,2]

Pinsent kinetics[1,2]

$$r_j = k_j^c \prod_{i=1}^{N} C_i^{\nu_i} \quad \forall\, j = 4{,}5$$

Aspen Plus

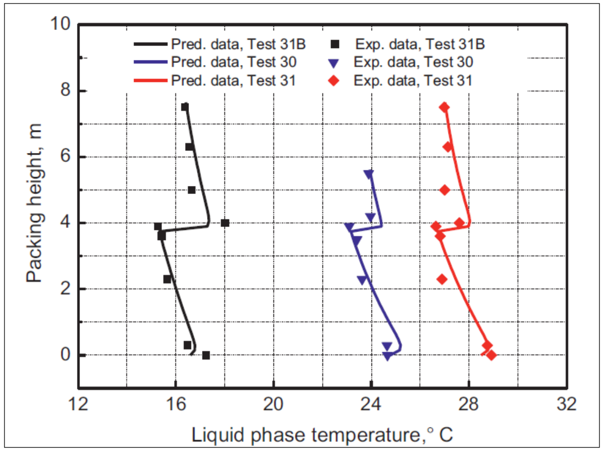
$$r_j = k_j^a \prod_{i=1}^{N} (x_i \gamma_i^*)^{\nu_i} \quad \forall\, j = 4, -4, 5, -5$$

Pinsent kinetics adapted to the new driving force (Thomsen model)

[1] Pinsent et al. *Trans Faraday Soc* 52 (1956) 1512-1520
[2] Pinsent et al. *Trans Faraday Soc* 52 (1956) 1594-1598

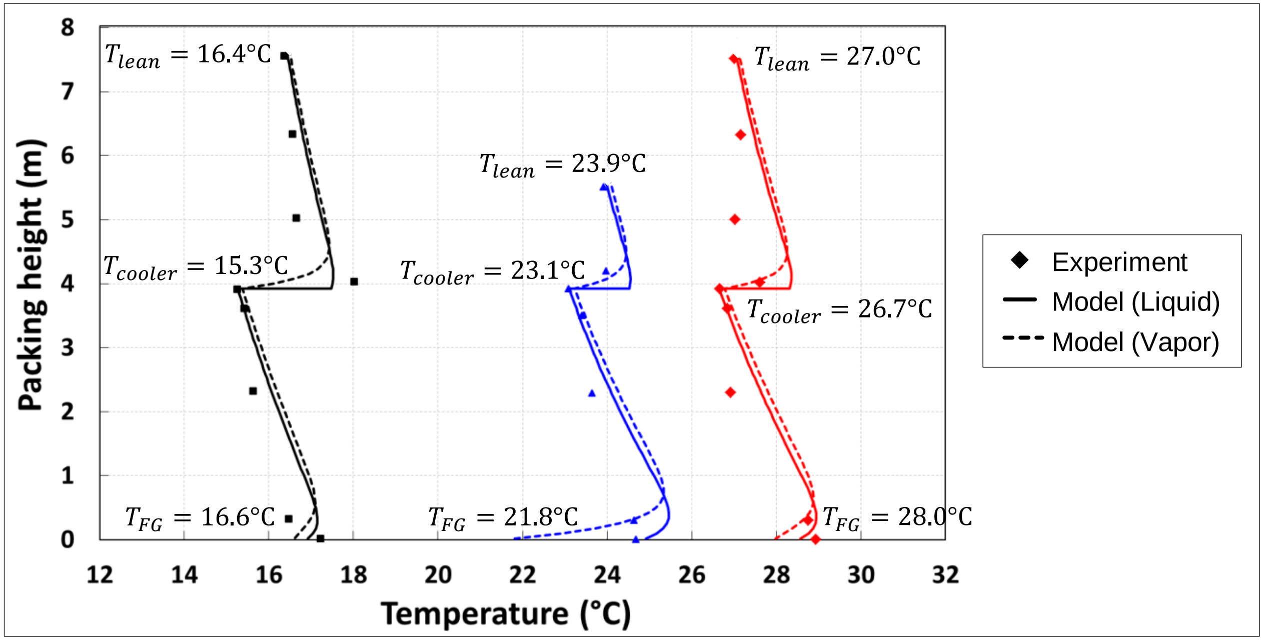
Rate-based model validation with CSIRO tests[1]

From literature[2]:
Rate-based model with
Chen thermodynamic **model**



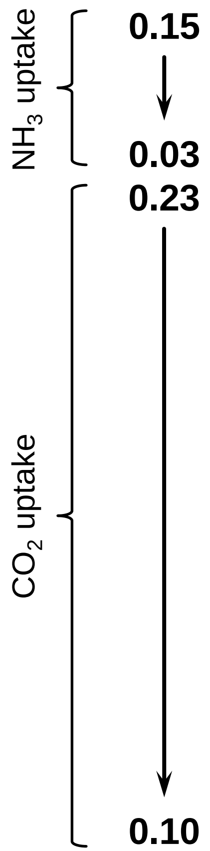
[1] Yu et al. *Chem Eng Res Des* 89 (2011) 1204-1215
[2] Qi et al. *Int J Greenh Gas Con* 17 (2013) 450-461

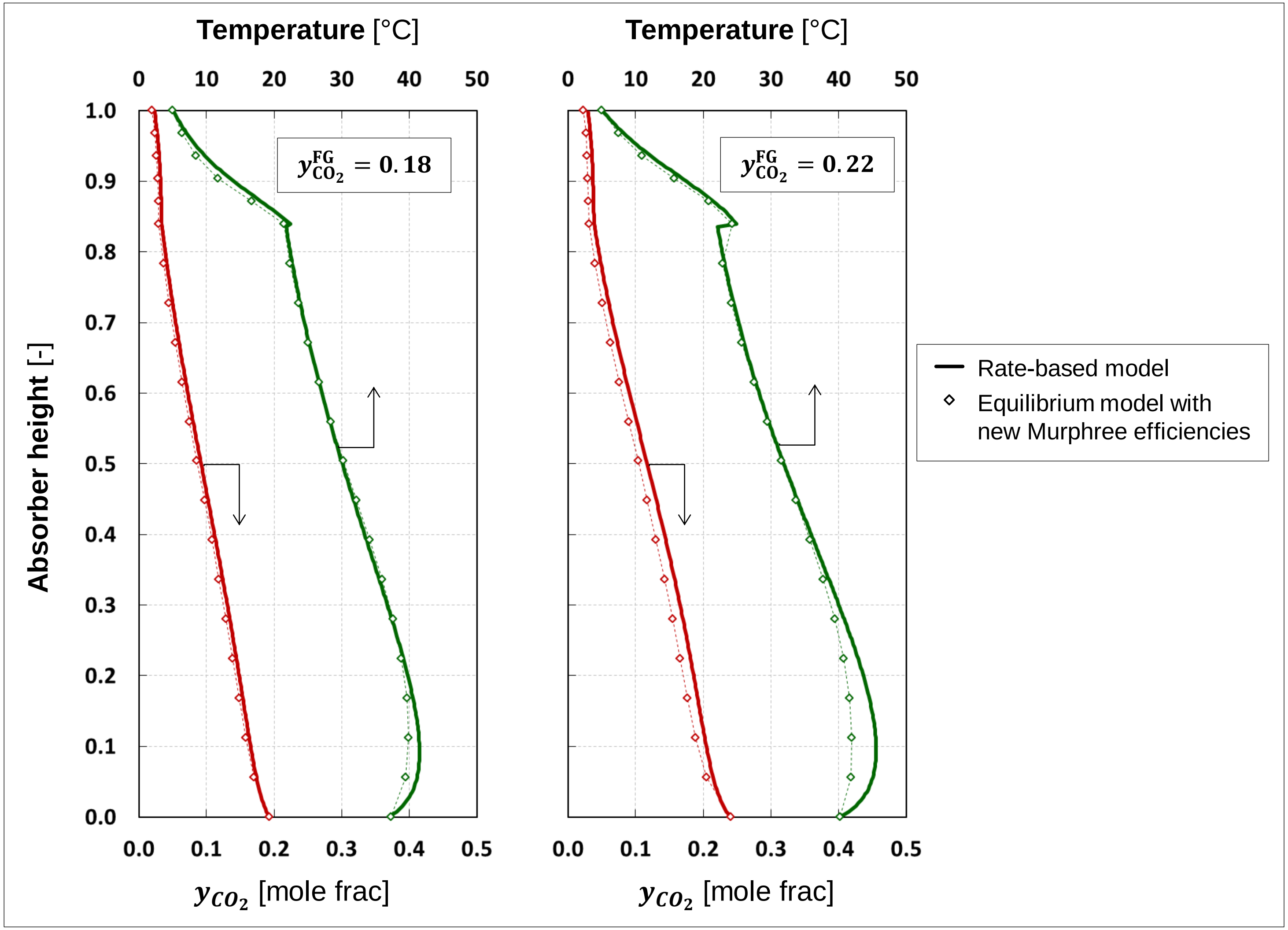
<u>This study:</u>
Rate-based model with
Thomsen thermodynamic **model** and **adapted kinetic parameters**



From rate-based to equilibrium-based simulations

Murphree efficiencies



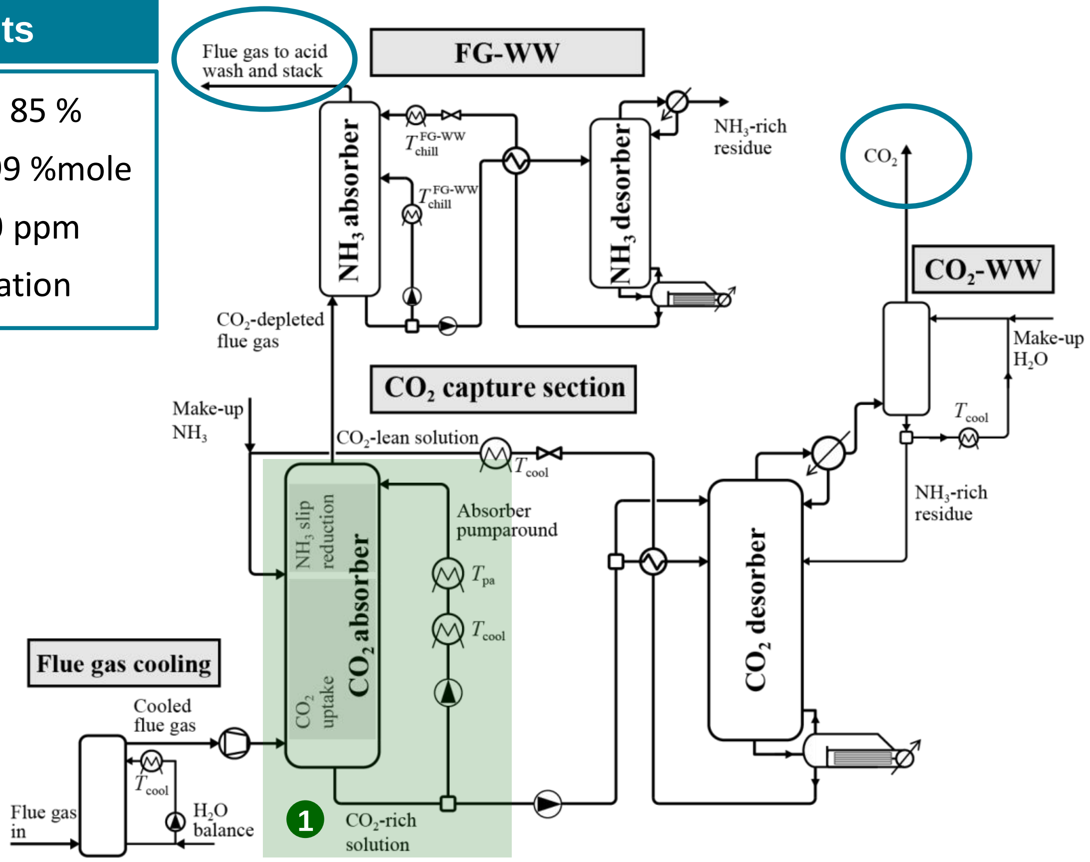


Heuristic optimization algorithm

1 Phase diagram–guided definition of feasible range of operating conditons

Specifications and constraints

- CO_2 capture > 85 %
- CO_2 purity > 99 %mole
- NH_3 slip < 200 ppm
- No solid formation



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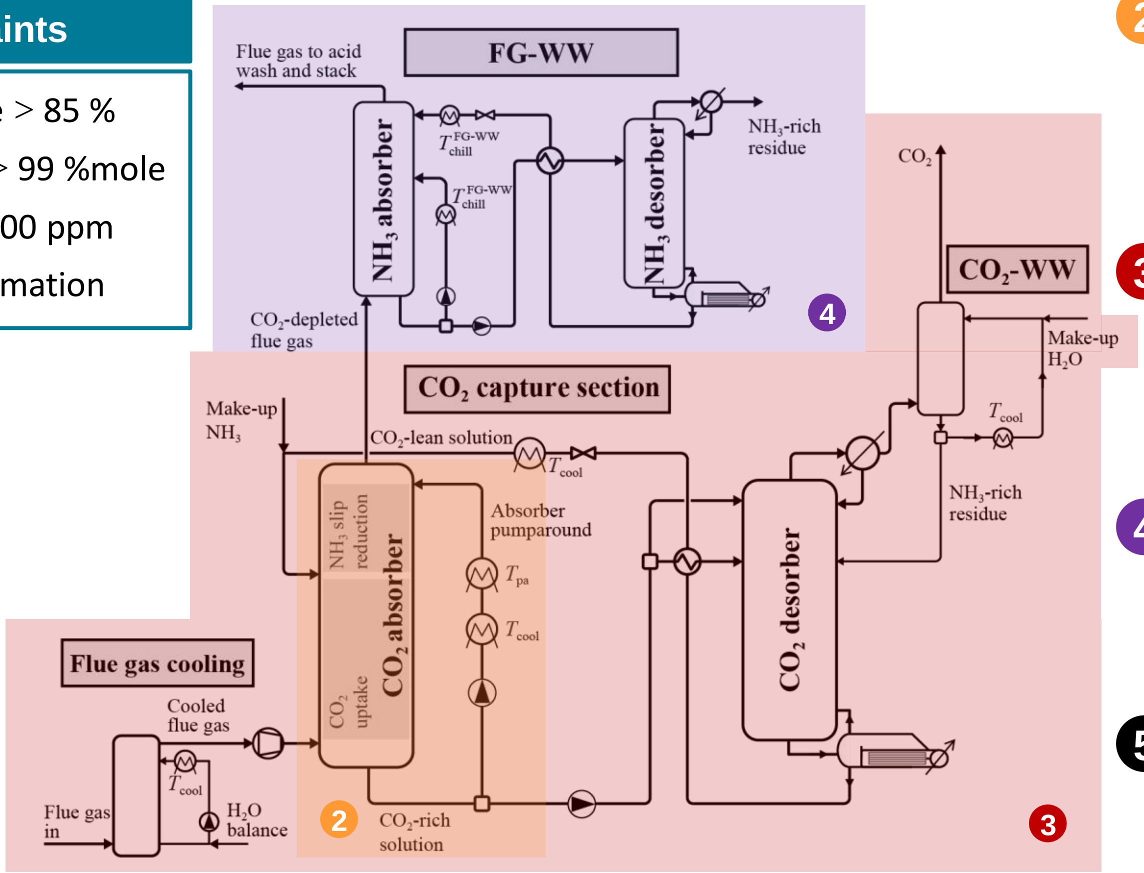
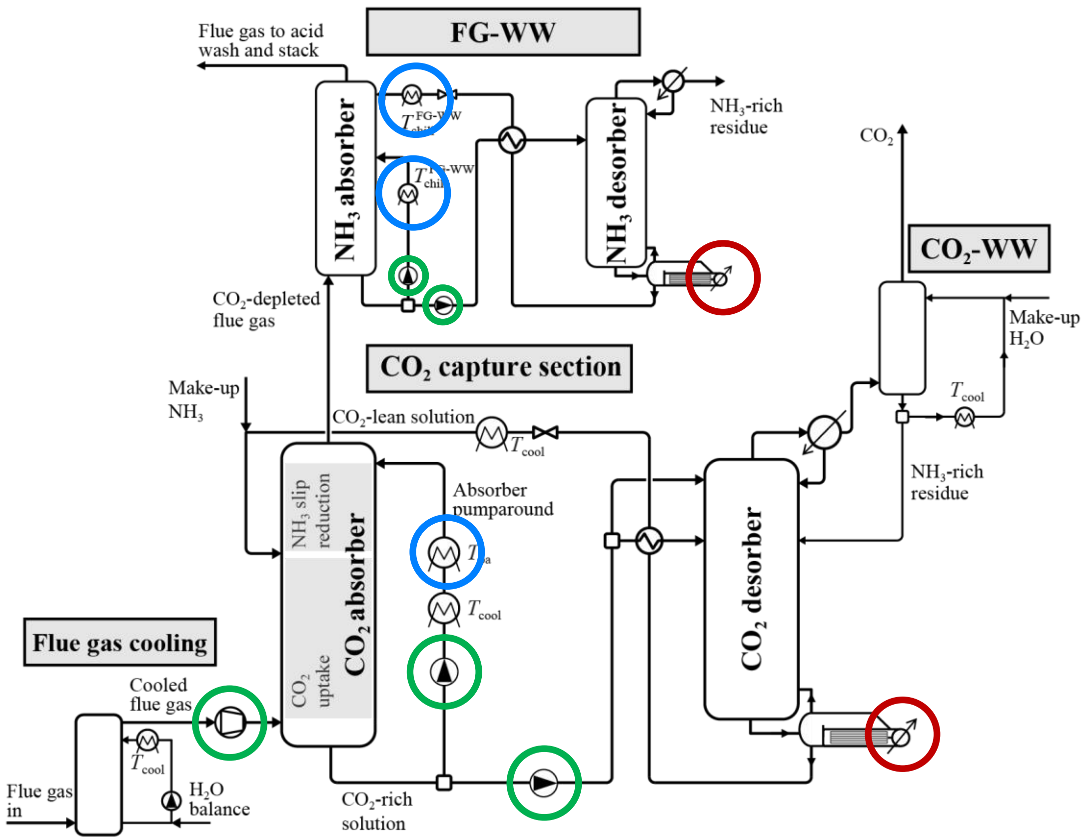


1. **Phase diagram–guided definition of feasible range of operating conditons**
2. **Automated sensitivity analysis**
   CO_2 absorber
   ~10^4 simulations
3. **Automated sensitivity analysis**
   CO_2 capture section
   ~10^4 simulations
4. **Rigorous optimization**
   FG-WW section
   ~10^3 simulations
5. **Objective function computation**
   ~10^3 simulations

Objective function

Total Specific Exergy Needs

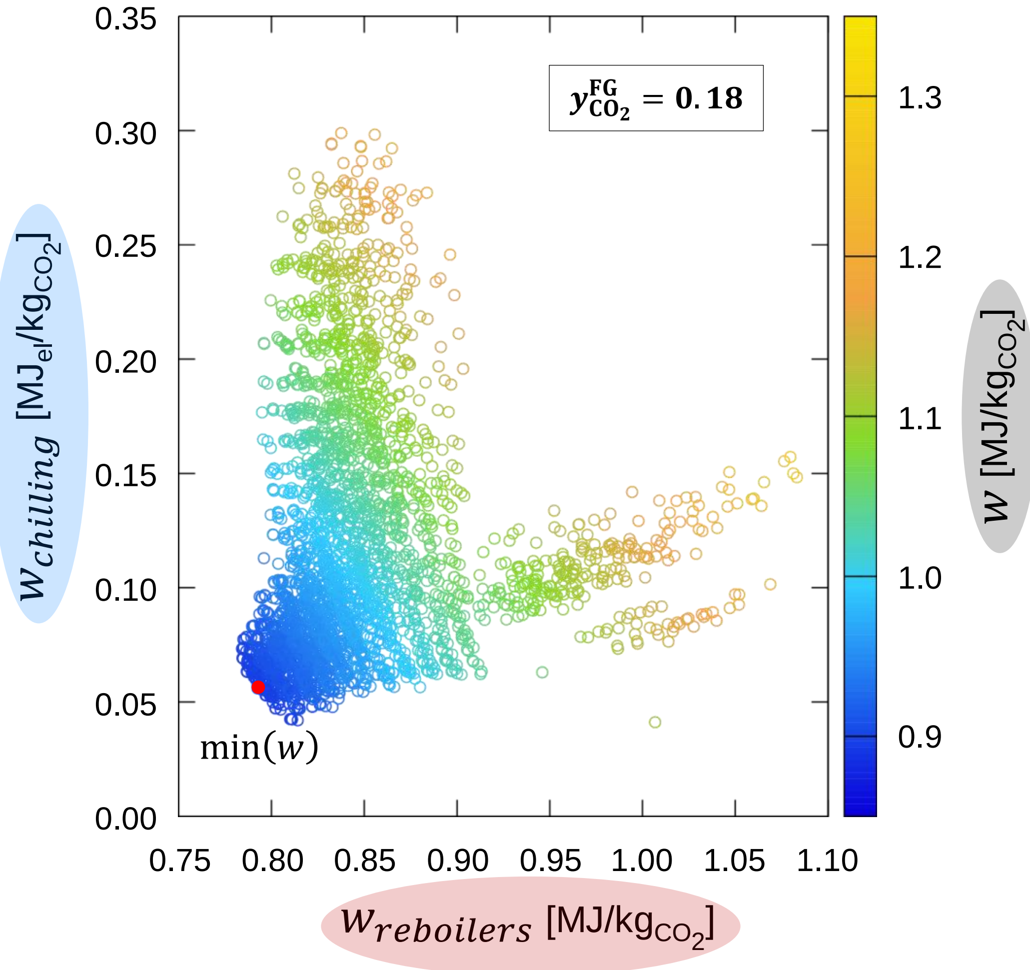
$$w = \frac{W_{reboilers} + W_{chilling} + W_{auxiliaries}}{m_{CO_2}^{abs}} \left[\frac{\text{MJ}}{\text{kg CO}_2\text{ captured}}\right]$$



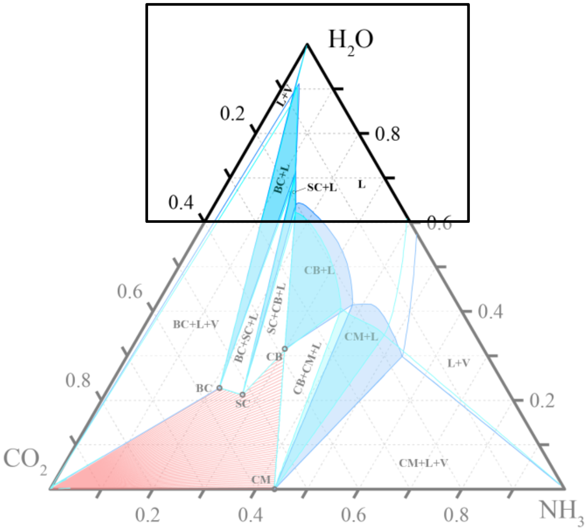
Heuristic optimization results

Total Specific Exergy Needs

$$w = \frac{W_{reboilers} + W_{chilling} + W_{auxiliaries}}{m_{CO_2}^{abs}} \left[\frac{\text{MJ}}{\text{kg CO}_2\text{ captured}}\right]$$

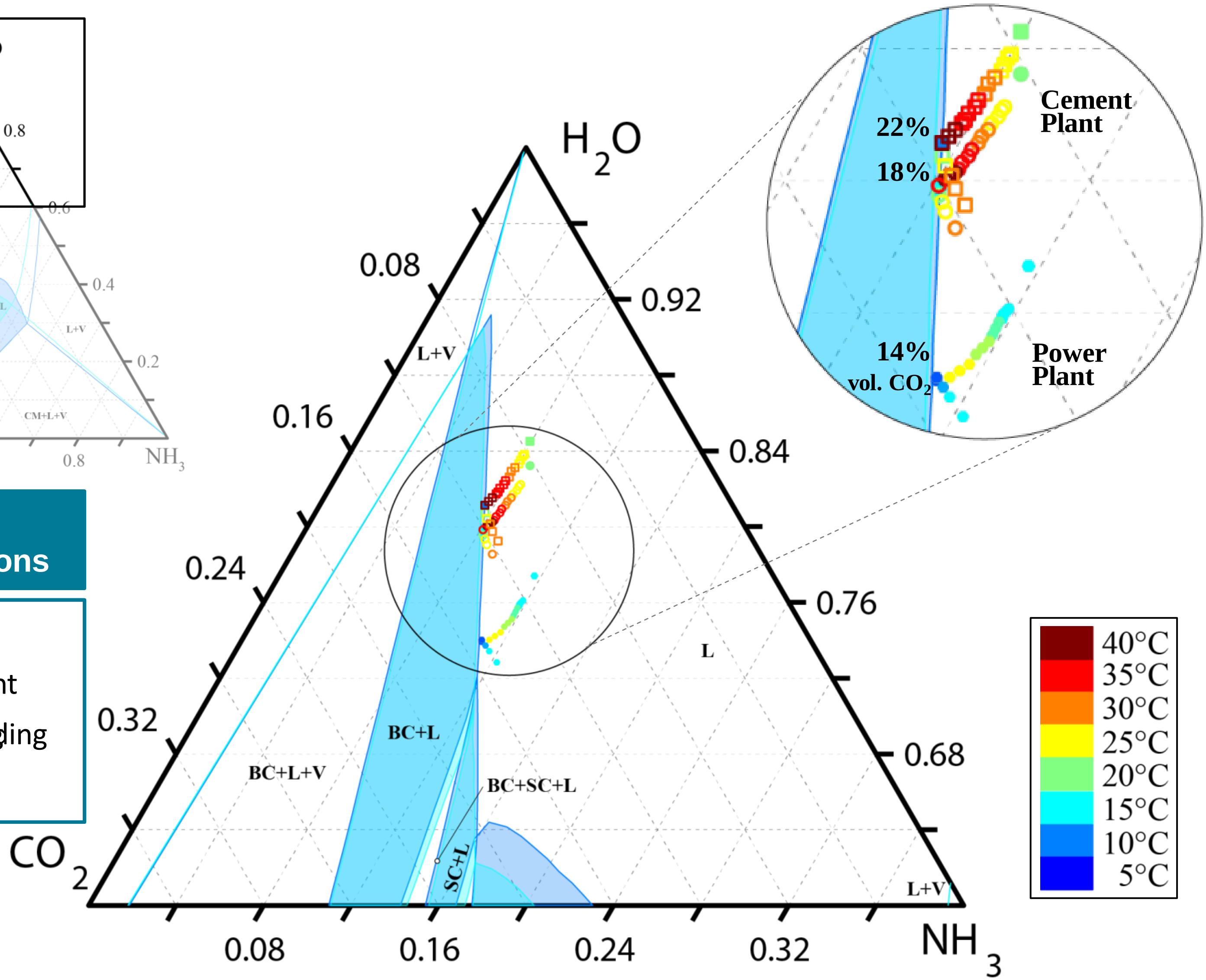


CO_2 absorber profiles for optimum operating conditions



Adaptation of operating conditions

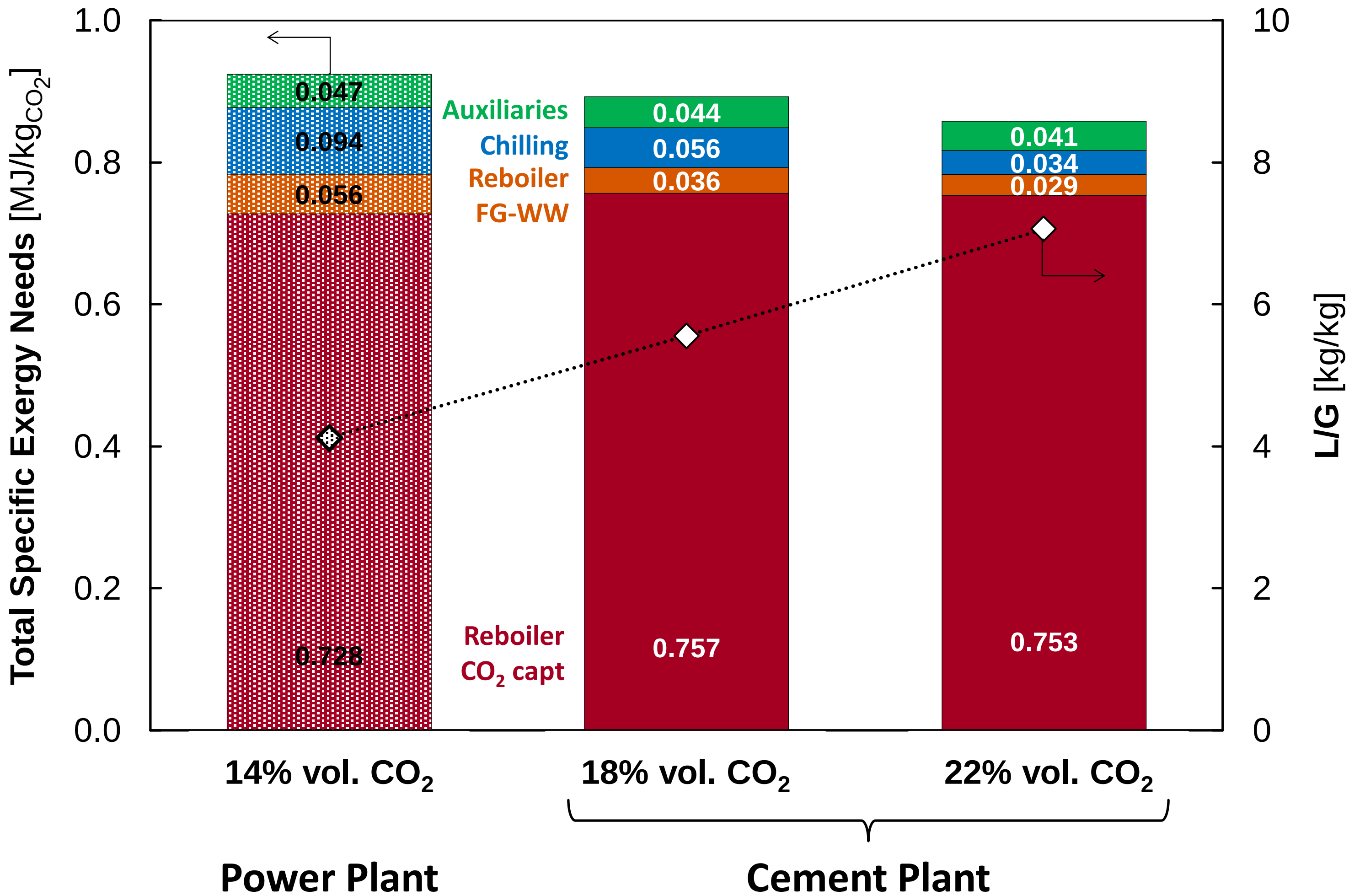
- **Higher L/G**
- Lower NH_3 content
- Constant CO_2 loading
- **Combination**



Comparison of results

Higher CO_2 concentration in the flue gas leads to:

- Lower exergy needs
- Increase in the L/G in the CO_2 absorber



Conclusions

- The **Chilled Ammonia Process can be applied** for CO_2 capture **to cement plants**

- A **rate-based model using Thomsen** thermodynamic **model** has been **validated** with pilot plant tests from the literature

- The **heuristic optimization approach** has **led to the optimum set of operating conditions** of the process, based on:
  - Assessment of the energy requirements
  - Equilibrium model
    - Thomsen thermodynamic model
    - Ad-hoc Murphree efficiencies for cement plant flue gas compositions

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement no 641185

This work was supported by the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract number 15.0160

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