ETH zürich

Development of an ammonia-based process for CO_2 capture in cement plants: absorption tests, rate-based modelling and process optimization

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Talk outline

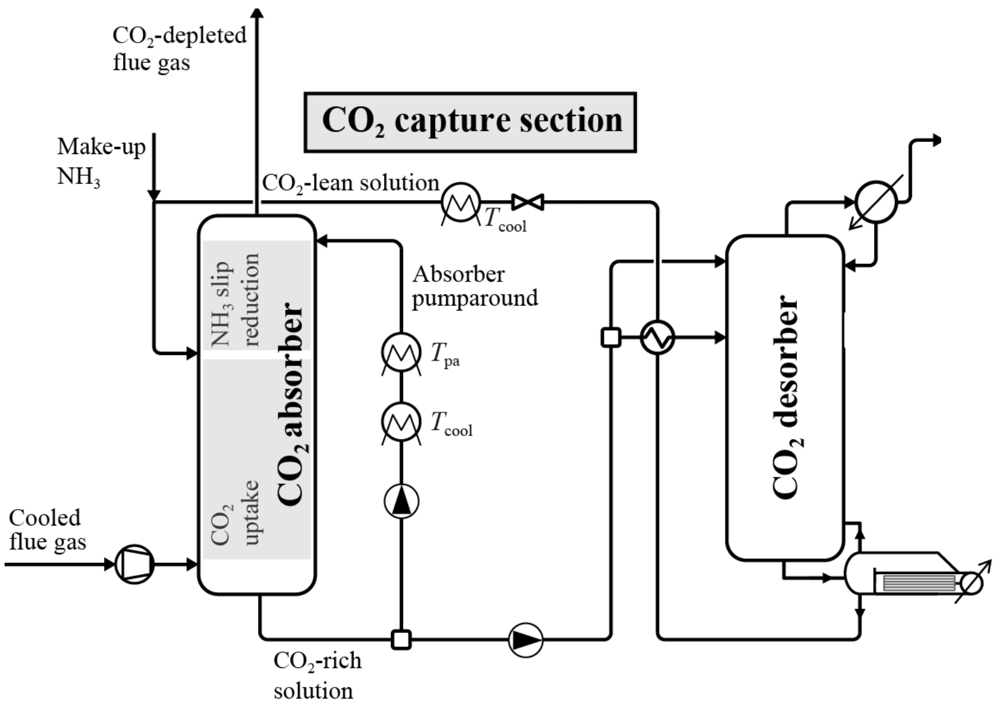
- **Introduction** and **scope** of the study
- **Model**
- **CAP** heuristic **optimization for cement plants**
- **Pilot plant tests** of the CO_2 absorber
- **Regression of kinetic parameters**
- **Conclusions**

CO_2 emissions from cement & the CAP

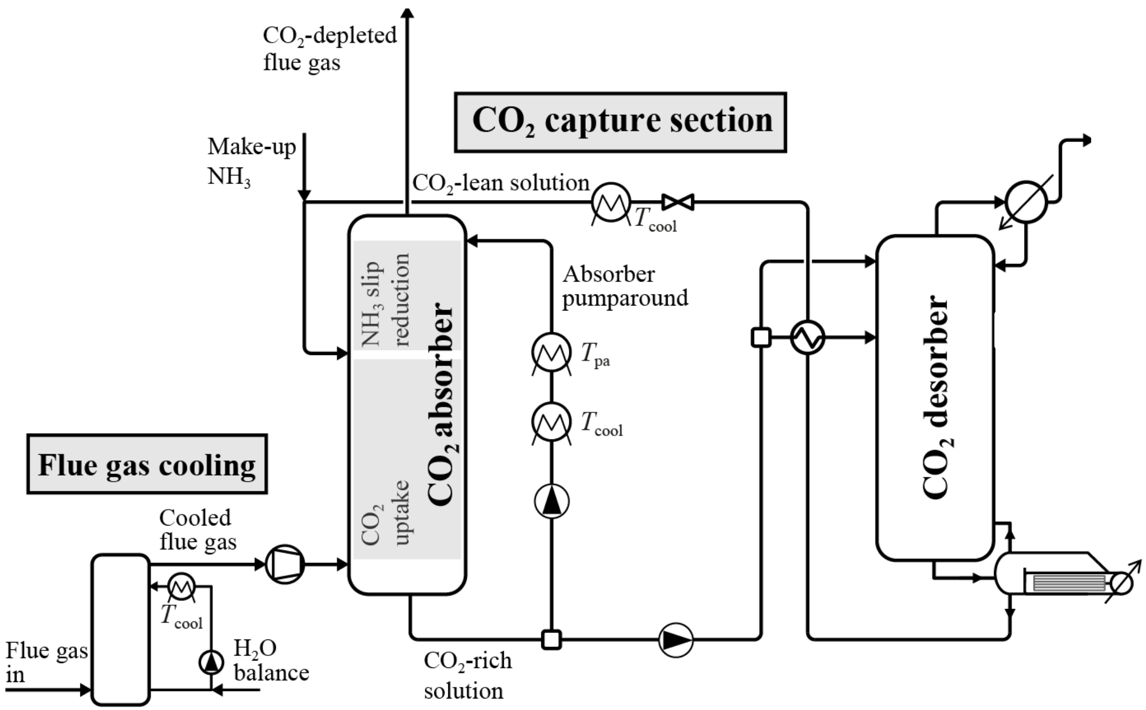
- 5% of global anthropogenic CO_2 emissions
- ~ 0.58 t CO_2/t cement (BAT)
  - ~ 50 – 60% process-related emissions ➔ **CCS required**

- 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

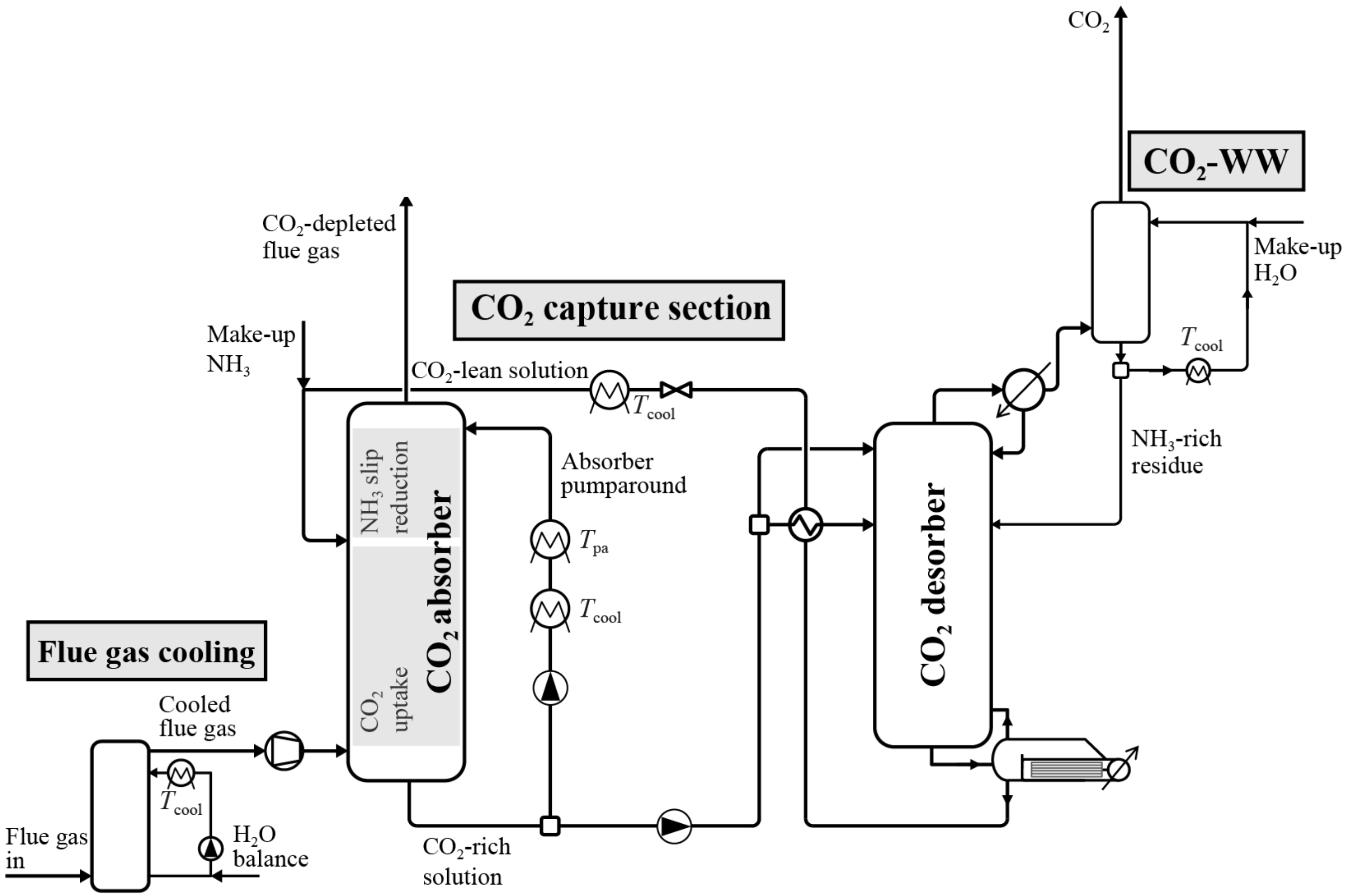
The Chilled Ammonia Process



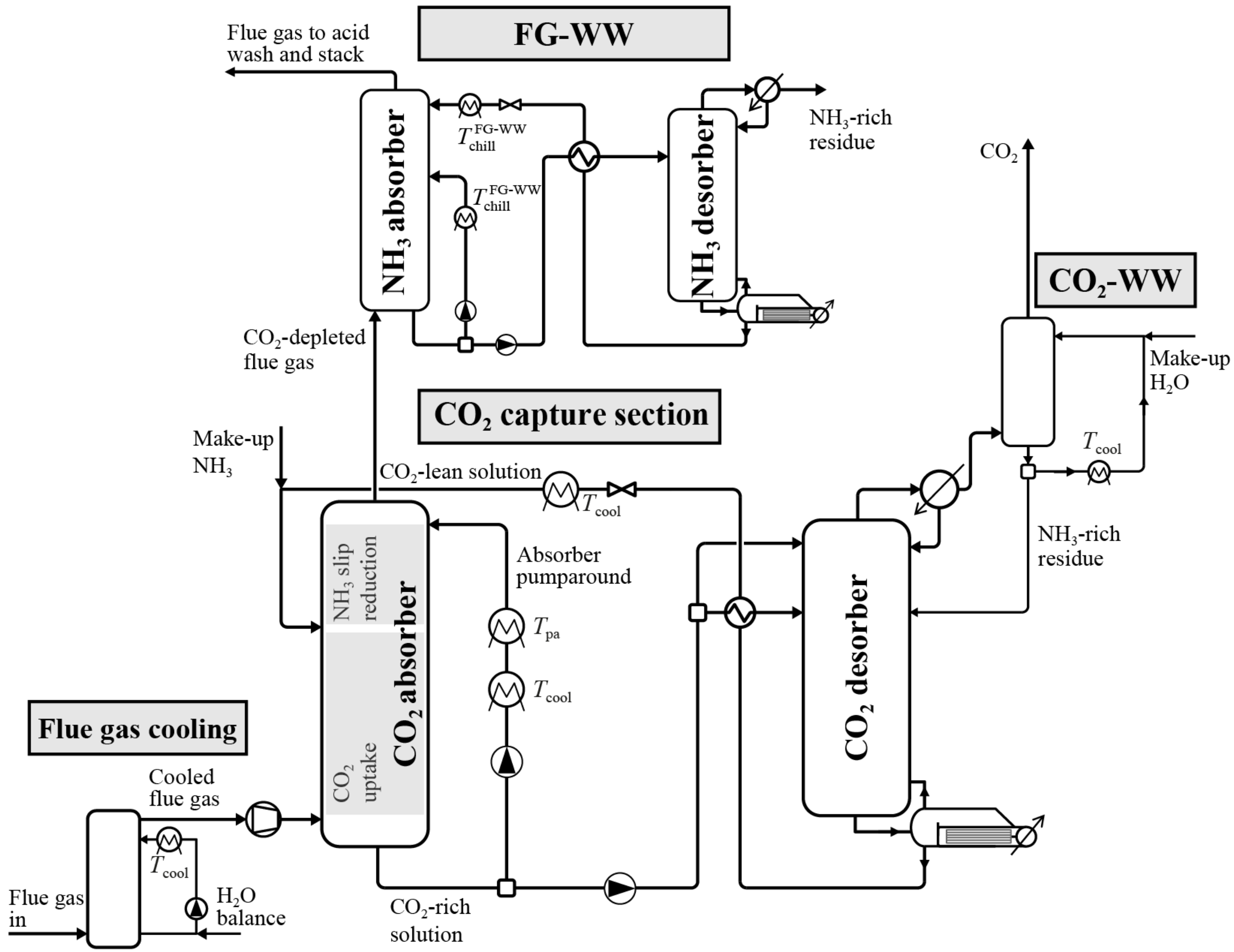
The Chilled Ammonia Process



The Chilled Ammonia Process



The Chilled Ammonia Process

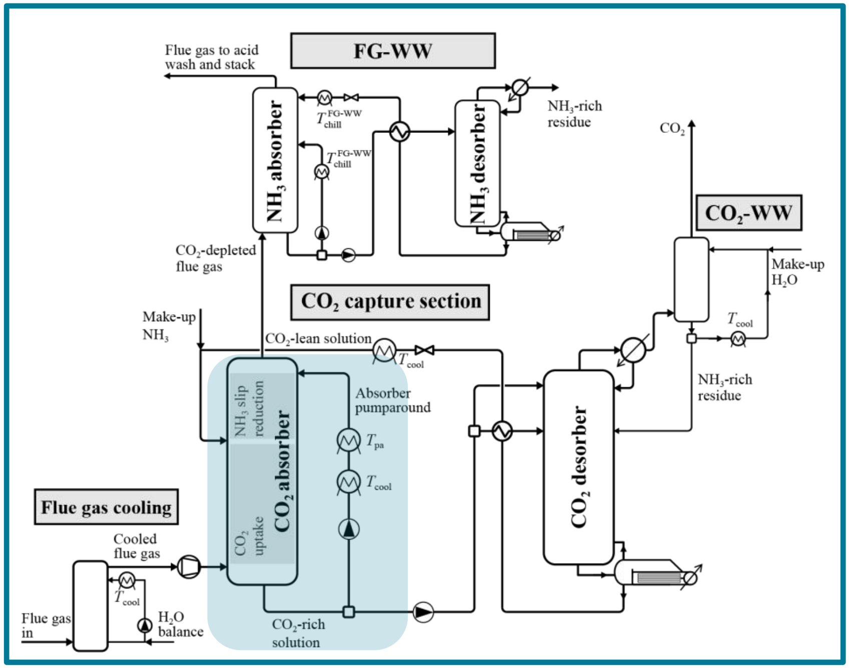


From power plants to cement plants

NG power plants
~ 4 %vol. CO_2

Coal-fired power plants
~ 14 %vol. CO_2

Cement plants
15 – 35%vol. CO_2



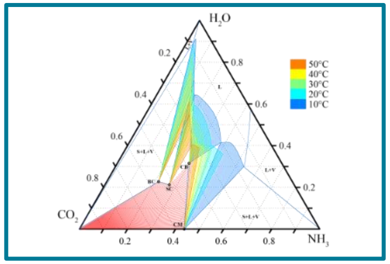
Adaptation of operating conditions

Model-based optimization

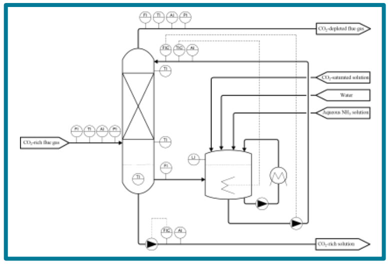
- Process complexity
- Heat integration
- **Thermodynamics**
- **Kinetics**

Scope of the study

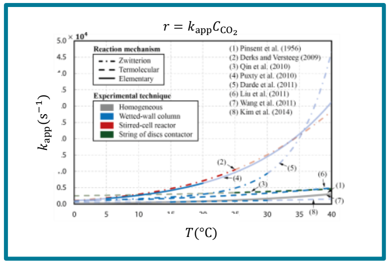
Equilibrium model (Aspen Plus)



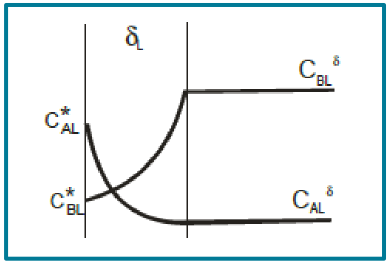
Pilot plant tests



Reaction kinetics



Rate-based model (Aspen Plus)



Power plant

Starting point

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

Cement plant

Ultimate goal

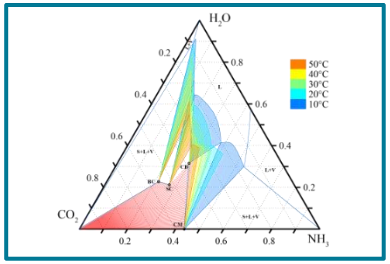
- **Thomsen model[1,2]**
- **Mass transfer resistance**
- **Reaction kinetics**

Model-based optimization

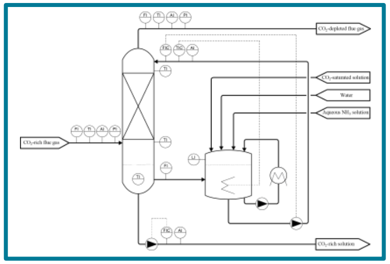
[1] Thomsen and Rasmussen *Chem Eng Sci* 54 (1999) 1787-1802
[2] Darde et al. *Ind Eng Chem Res* 49 (2010) 12663-74
[3] Sutter et al. *Faraday Discuss* 192 (2016) 59-83
[4] Jilvero et al. *Ind Eng Chem Res* 53 (2014) 6750-6758

Scope of the study

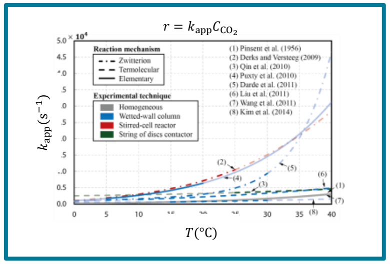
Equilibrium model (Aspen Plus)



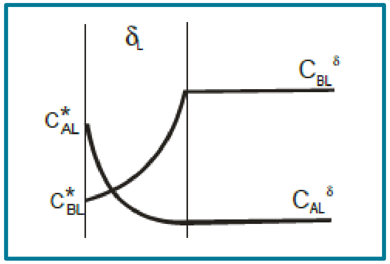
Pilot plant tests



Reaction kinetics



Rate-based model (Aspen Plus)



Power plant

Starting point

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

Cement plant

Ultimate goal

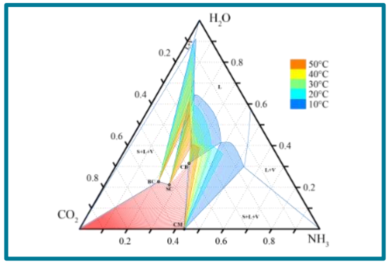
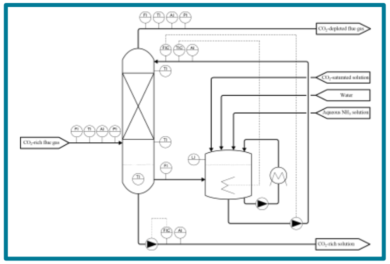
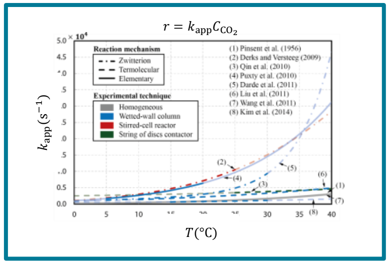
- Thoms mod 2]
- Mass tr istance
- React

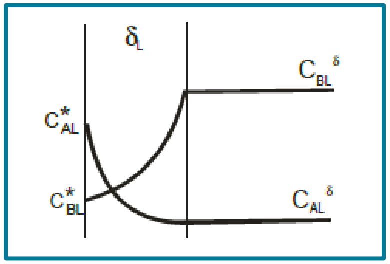
Model-based optimization

[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

Scope of the study

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



Power plant

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

2
- Model validation with CSIRO pilot tests

1
- Literature research

3
- Thomsen model[1,2]
- Validated kinetic model

Cement plant

4
- Ad-hoc Murphree efficiencies for cement plants
- Thomsen model[1,2]

5 Model-based optimization

6
- Definition of test matrix
- Cement-like flue gas composition

7
- Regression of kinetic parameters

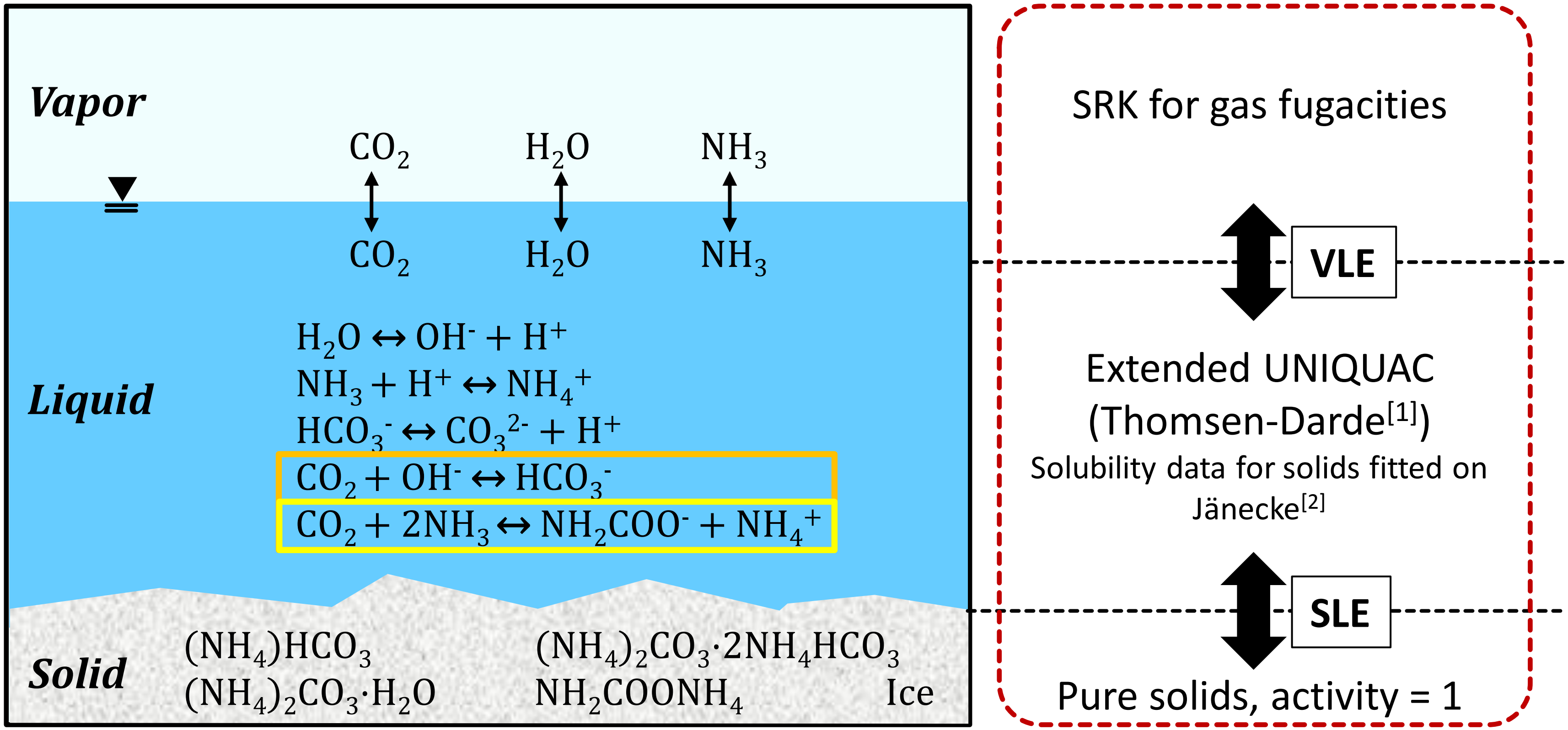
Ultimate goal
- Thomsen model[1,2]
- Mass transfer resistance
- Reaction kinetics

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

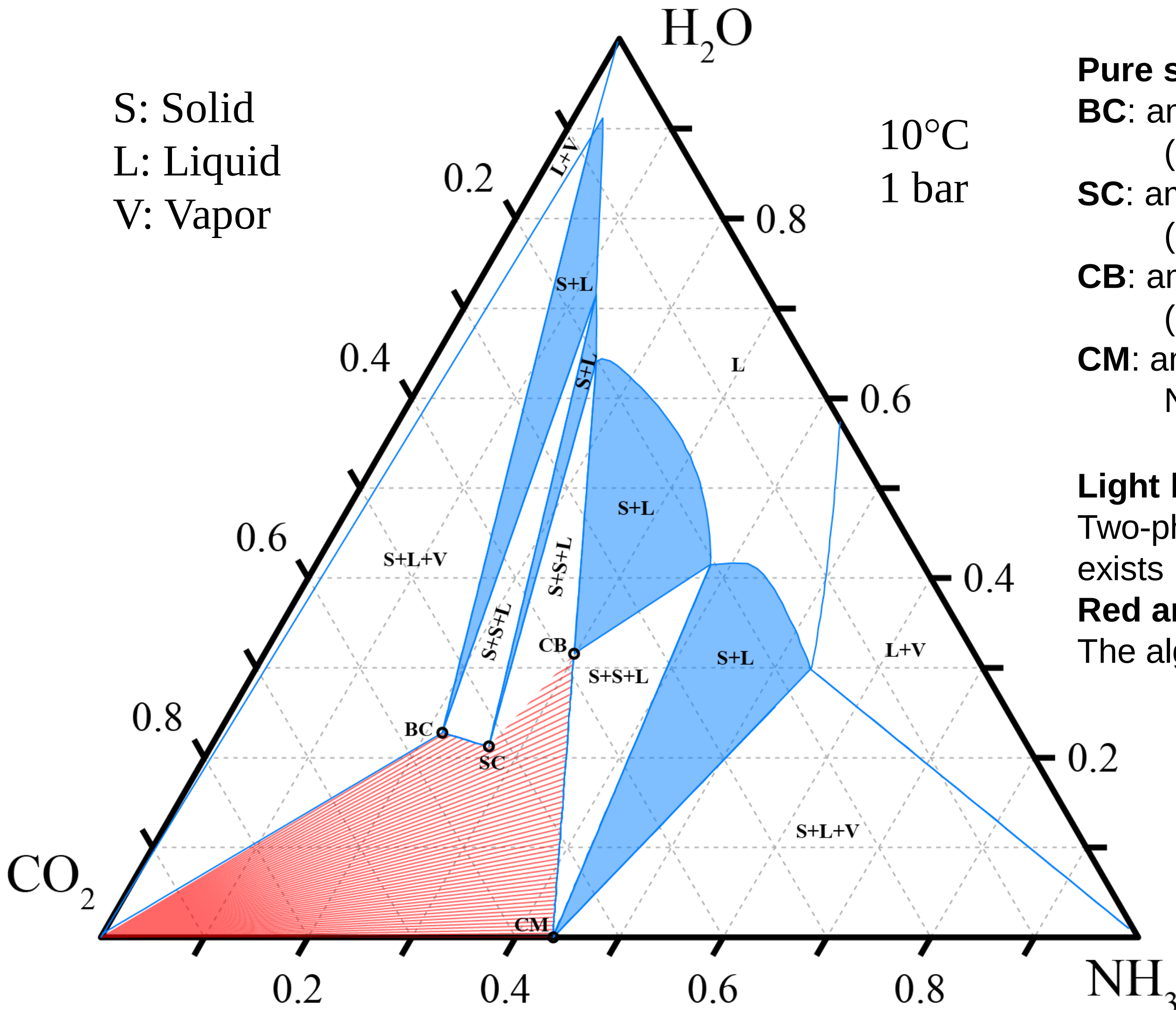
Thomsen model to predict the system thermodynamics



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

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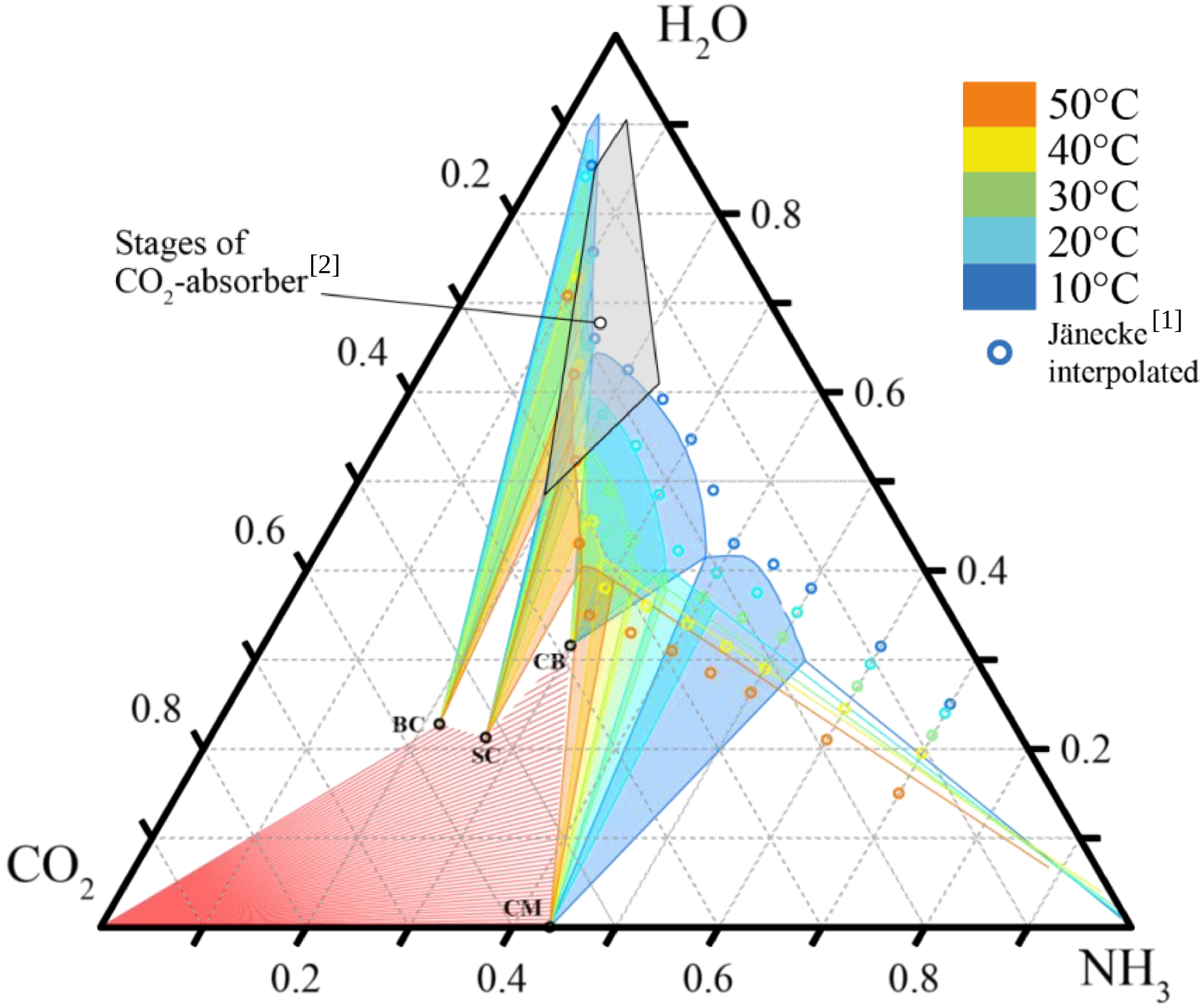
Phase diagram: CO_2-NH_3-H_2O system



[1] Jänecke *Z Elektrochem* 35 (1929) 9:716-728

[2] Sutter et al. *Chem Eng Sci* 133 (2015) 170-180

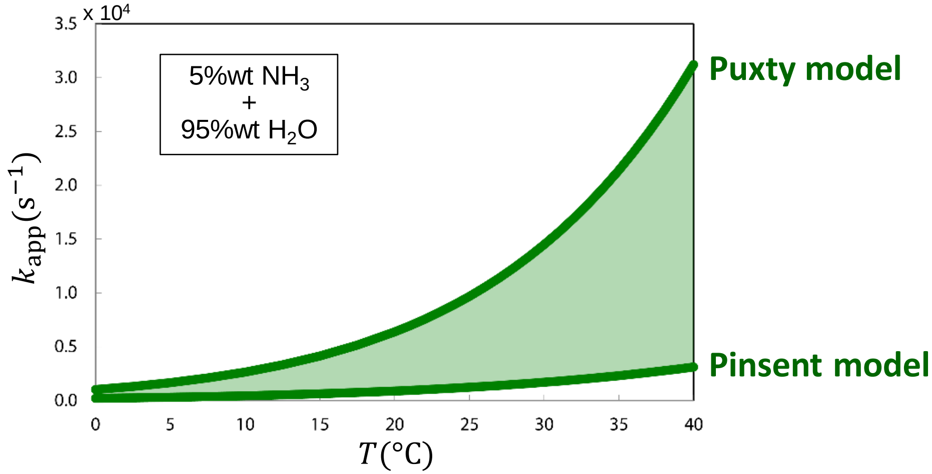
Rate-based model validation with CSIRO tests

$$CO_2 + 2NH_3 \xrightarrow{k_{cm}} NH_2COO^- + NH_4^+$$

$$r_{cm} = k_{app} C_{CO_2}$$

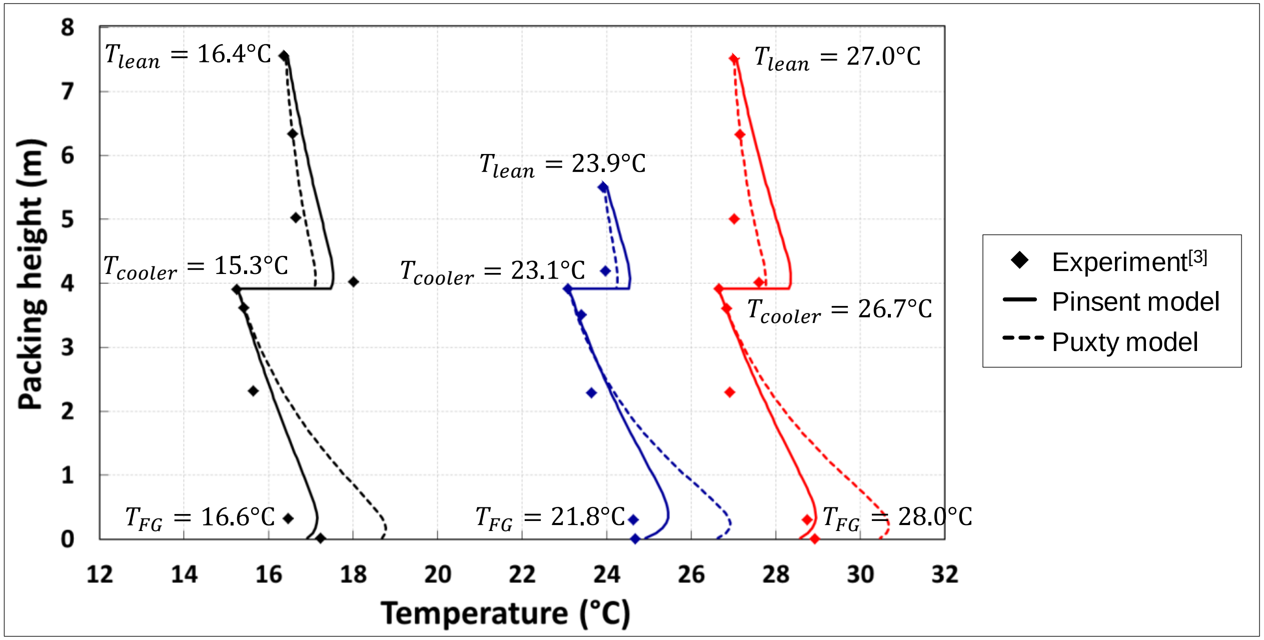
[1] Pinsent et al. *Trans Faraday Soc.* 52 (1956) 1594-1598

[2] Puxty et al. *Chem Eng Sci.* 65 (2009) 915-922



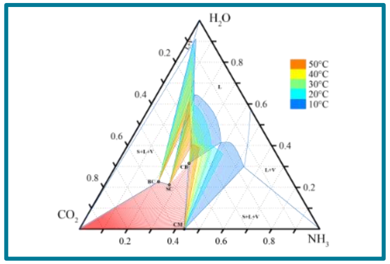
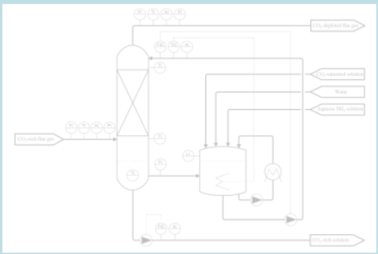
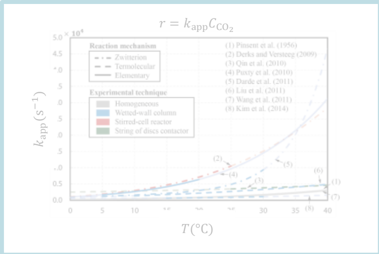
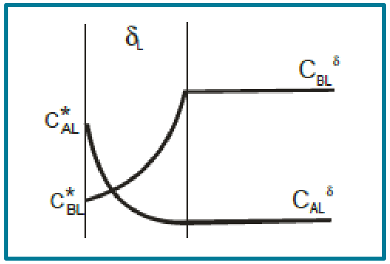
Rate-based model with:

- **Thomsen model**
- **Reaction kinetics:**
  - Pinsent model
  - Puxty model



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

From the power plant to the cement plant

	Equilibrium model (Aspen Plus)	Pilot plant tests	Reaction kinetics	Rate-based model (Aspen Plus)
				
Power plant	**Starting point** ▪ Thomsen model ▪ Murphree effs. for power plants from literature[3,4]	**2** ▪ Model validation with CSIRO pilot tests	**1** ▪ Literature research	**3** ▪ Thomsen model ▪ Pinsent model
Cement plant	**4** ▪ Ad-hoc Murphree efficiencies for cement plants ▪ Thomsen model	**6** ▪ Definition of test matrix ▪ Cement-like flue gas composition	**7** ▪ Regression of kinetic parameters	**Ultimate goal** ▪ Thomsen model ▪ Mass transfer resistance ▪ Reaction kinetics
	5 Model-based optimization			Model-based optimization

First CAP heuristic optimization for cement plants

Total Specific Exergy Needs

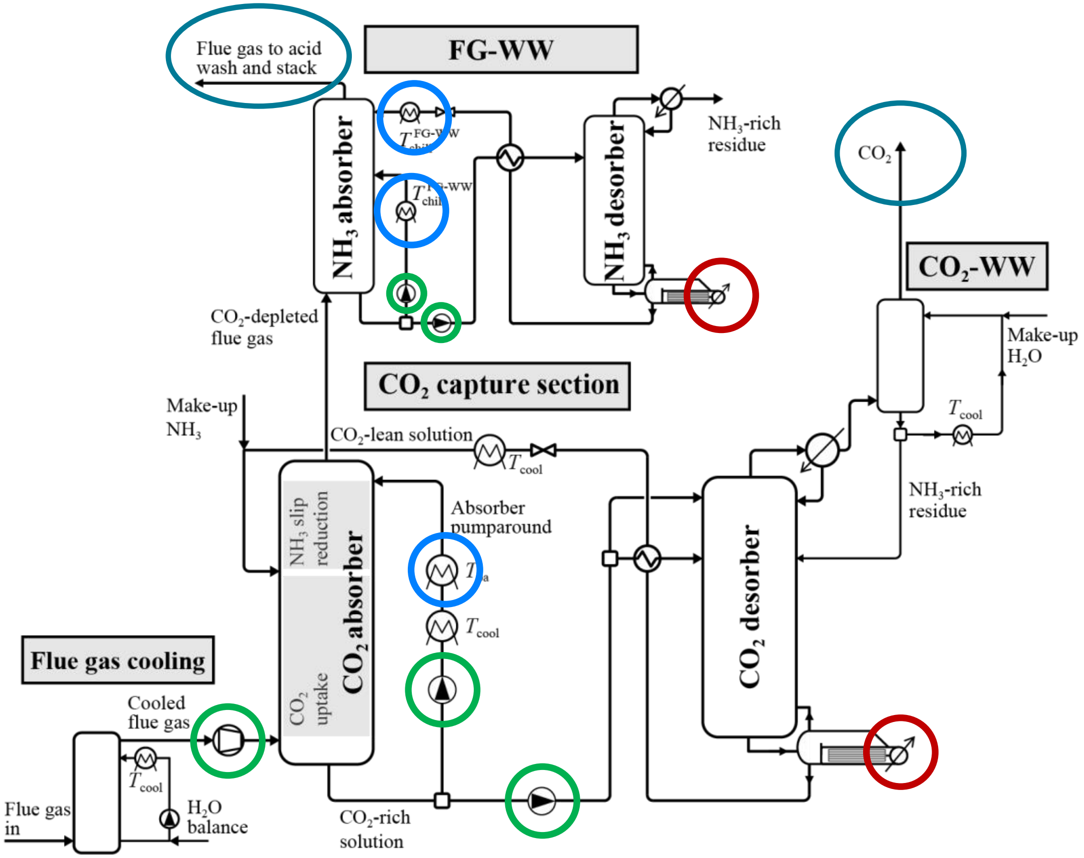
$$w = \frac{W_{\text{reboilers}} + W_{\text{chilling}} + W_{\text{auxiliaries}}}{m_{\text{CO}_2}^{\text{abs}}} \left[\frac{\text{MJ}}{\text{kg CO}_2\text{ captured}}\right]$$

Operating conditions varied in the CO_2 absorber

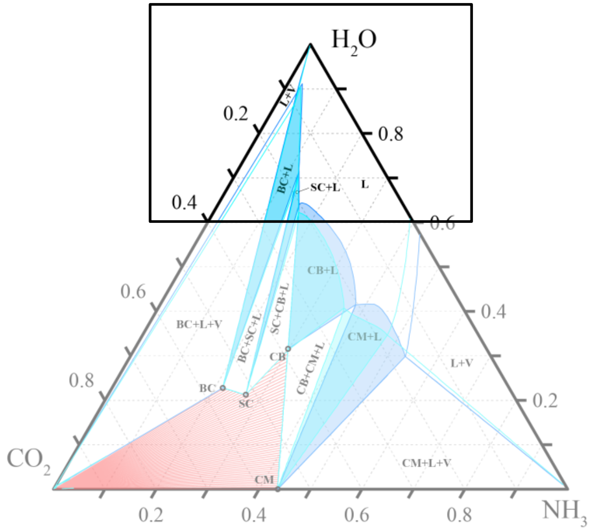
- L/G
- CO_2 loading
- NH_3 concentration
- Pumparound:
  - Temperature
  - Split fraction

Specifications and constraints

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

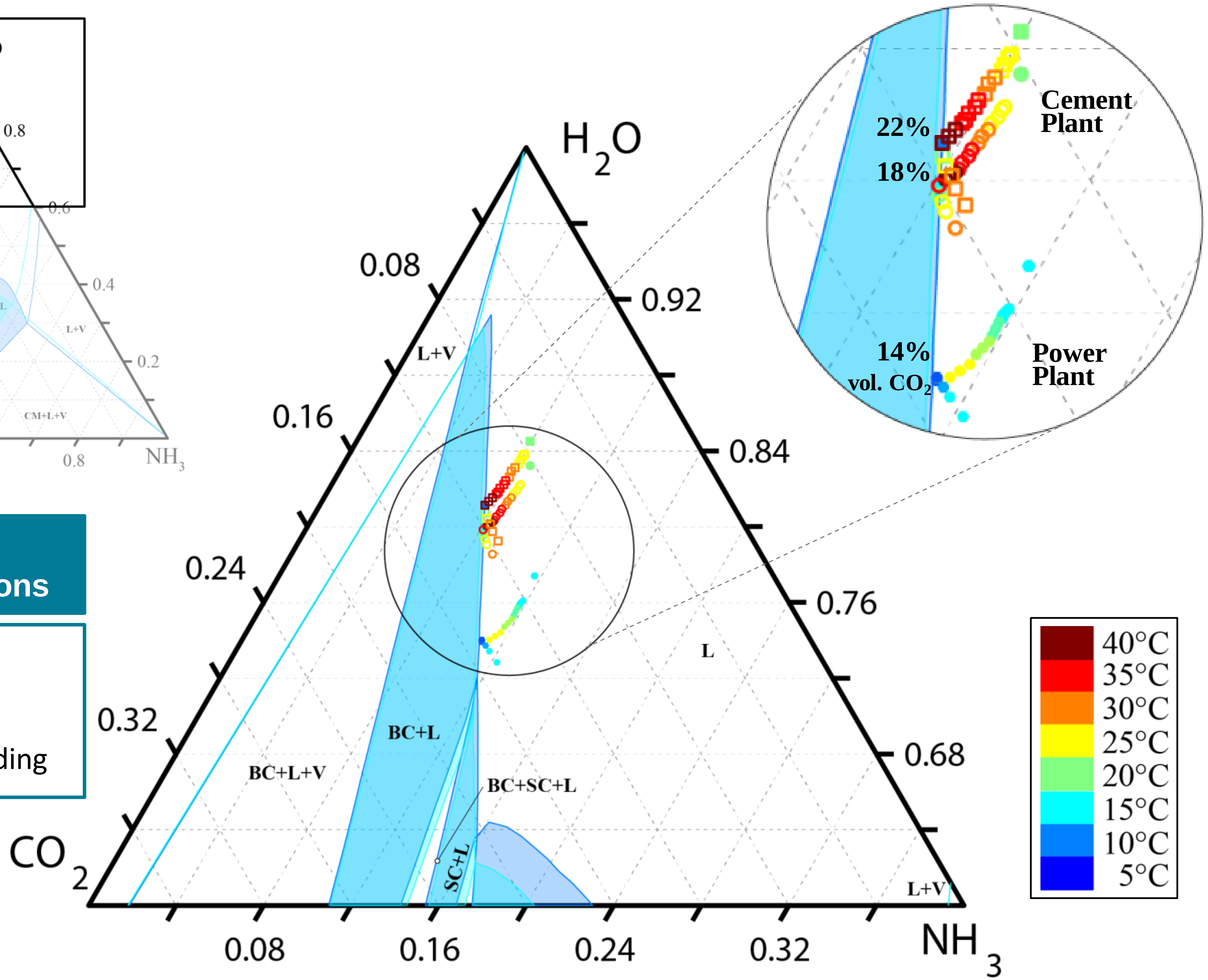


CO_2 absorber profiles for optimum operating conditions



Adaptation of operating conditions

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



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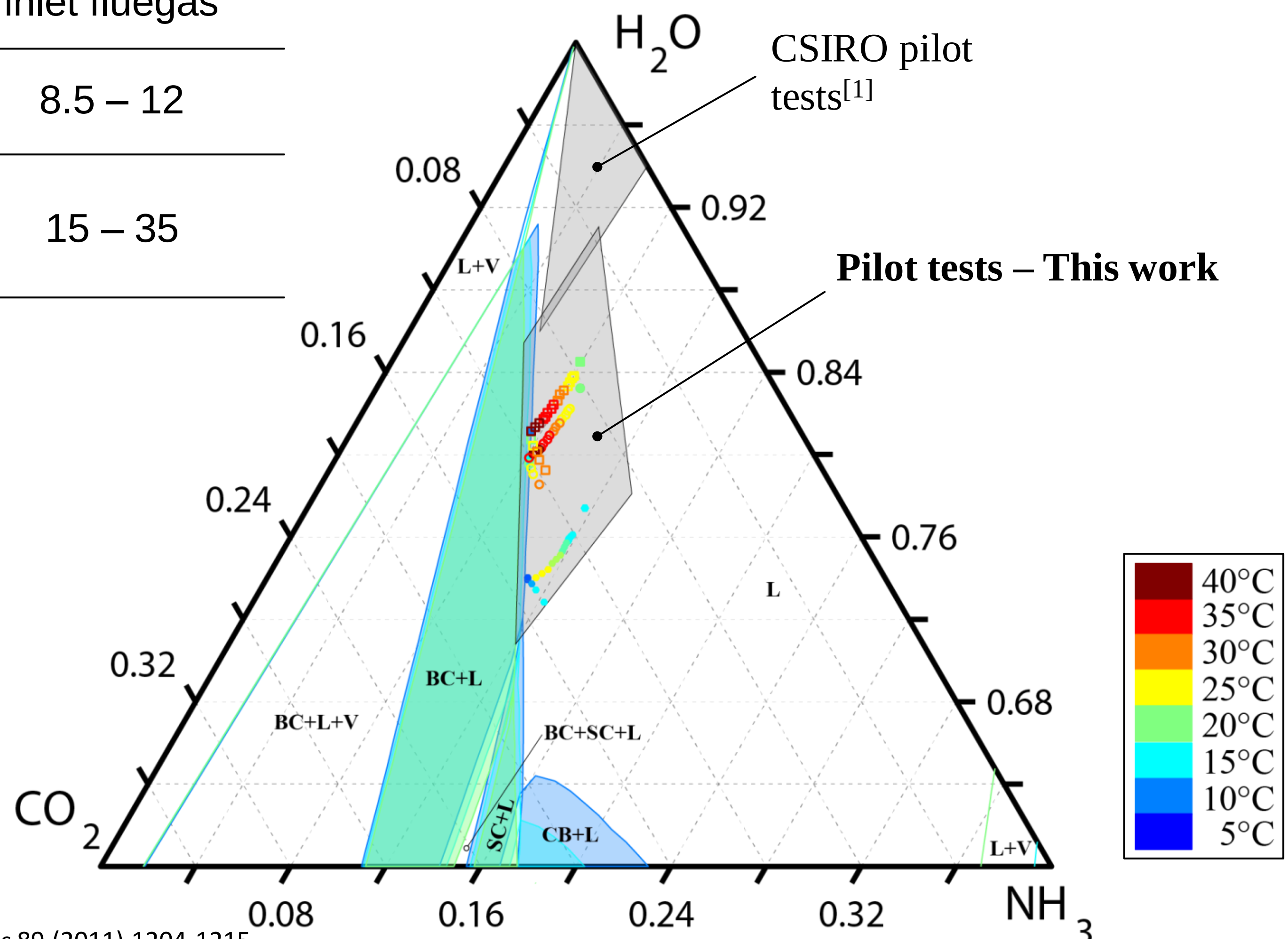
Definition of the test matrix for new absorber pilot tests

	%vol CO_2 in the inlet fluegas
CSIRO[1]	8.5 – 12
This work	15 – 35



[1] Yu et al. *Chem Eng Res Des* 89 (2011) 1204-1215

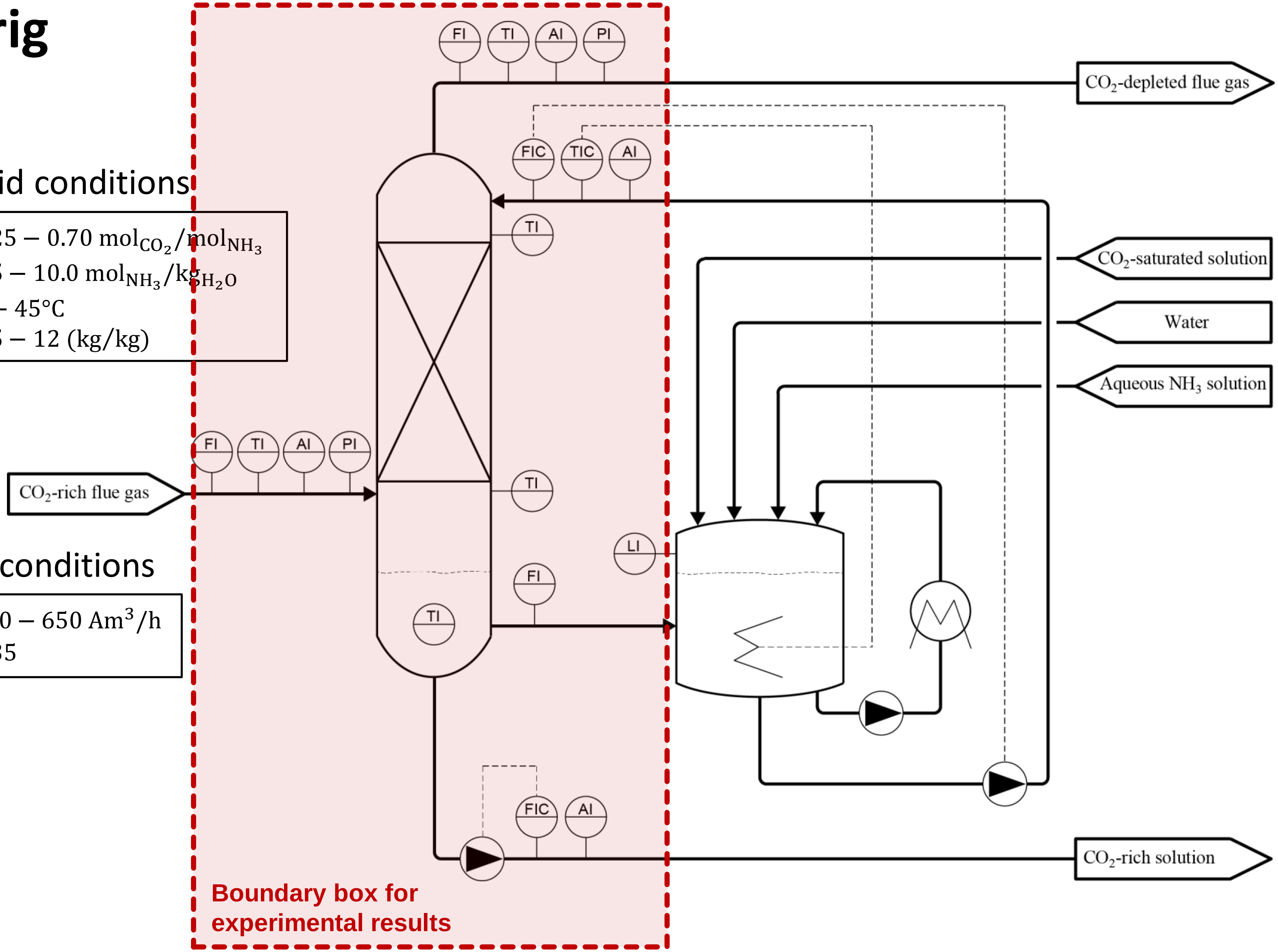
Test rig

Inlet liquid conditions

$l_{CO_2}^{in} = 0.25 - 0.70\ \mathrm{mol_{CO_2}/mol_{NH_3}}$
$m_{NH_3}^{in} = 3.5 - 10.0\ \mathrm{mol_{NH_3}/kg_{H_2O}}$
$T_L^{in} = 5 - 45°C$
$L/G = 2.5 - 12\ \mathrm{(kg/kg)}$

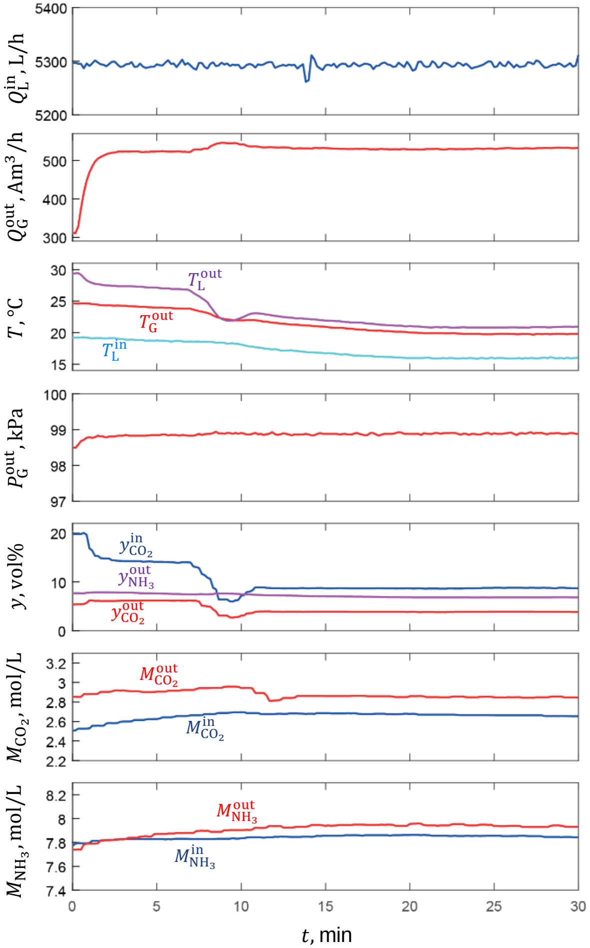
Inlet gas conditions

$Q_G^{in} = 400 - 650\ \mathrm{Am^3/h}$
$y_{CO_2}^{in} \leq 0.35$



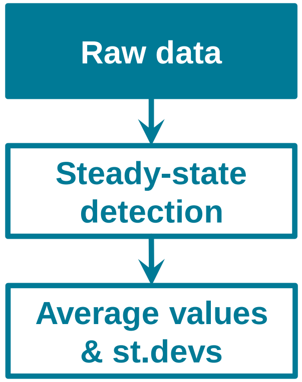
Systematic treatment of pilot raw data

Raw data

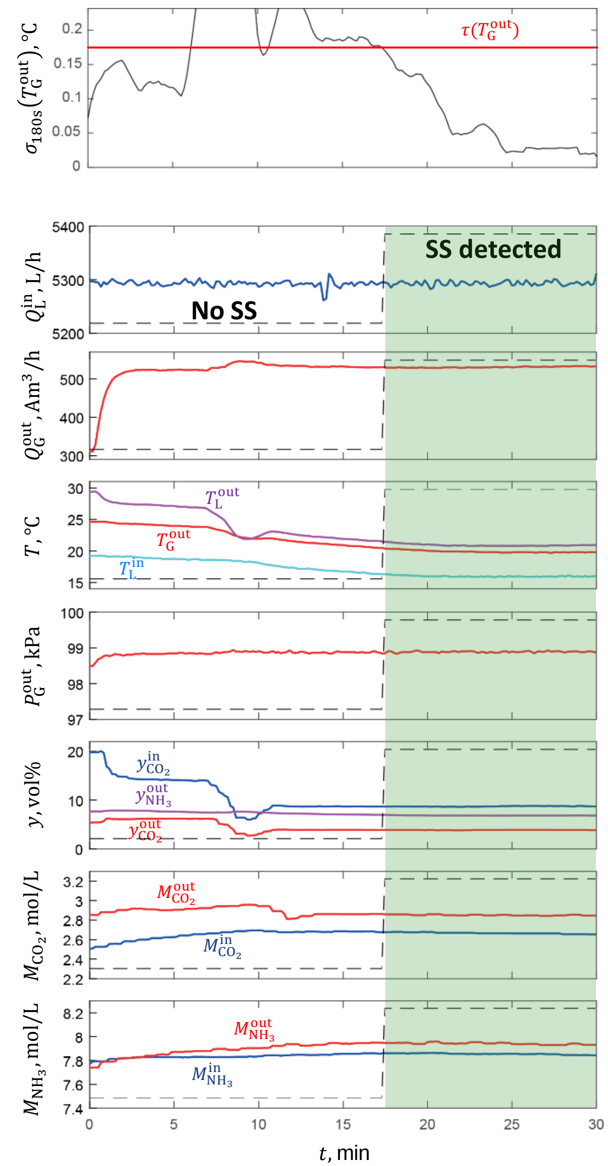


[1] Martínez-Maradiaga et al. *Appl Therm Eng.* 51 (2013) 1170-1180

Systematic treatment of pilot raw data

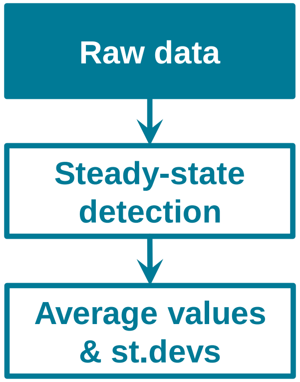


- Methodology based on a moving window[1]

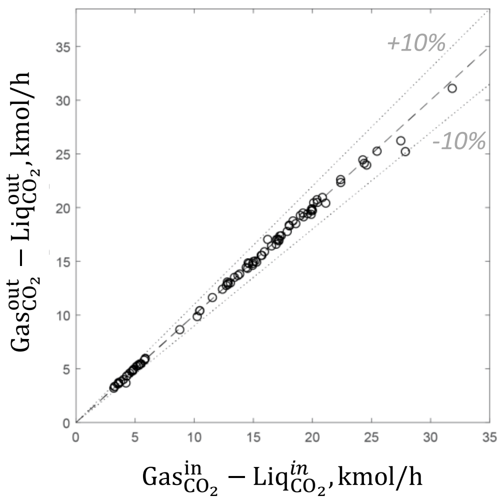


[1] Kim et al. *Int J Refrig.* 31 (2008) 790-799

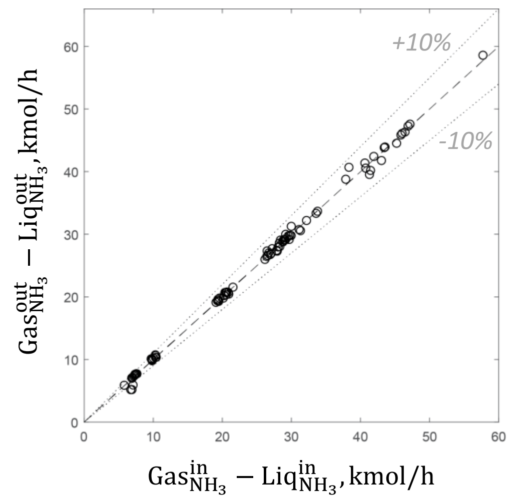
Systematic treatment of pilot raw data



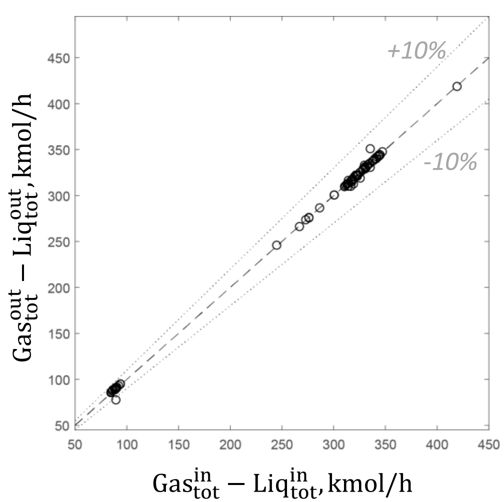
CO_2 mass balance



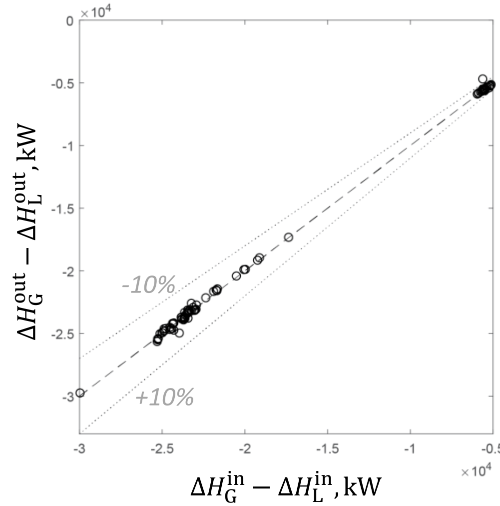
NH_3 mass balance



Total mass balance



Energy balance



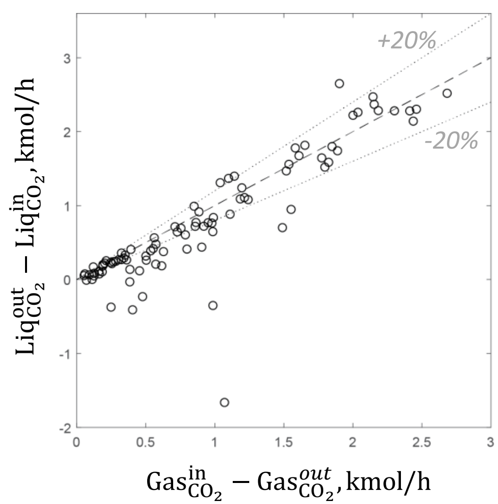
Systematic treatment of pilot raw data

Raw data → **Steady-state detection** → **Average values & st.devs**

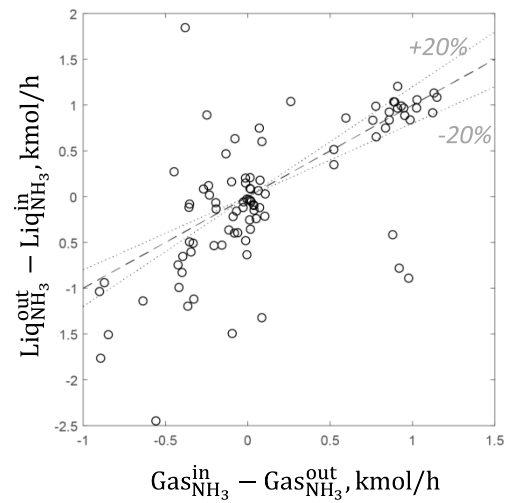
- Malfunctioning instruments?
- Deceptive measurements?
- Unreliable experiments?

Which experiments and measurements can we trust?

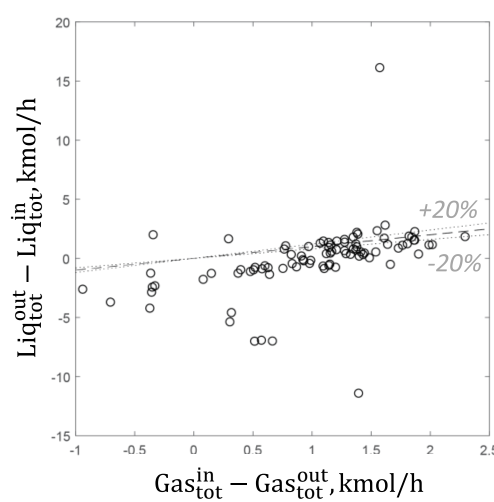
CO_2 mass balance



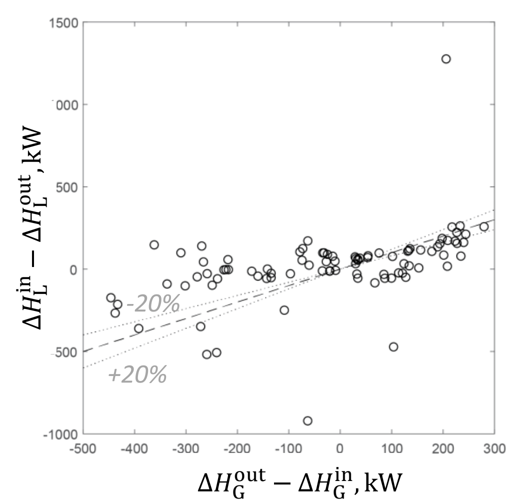
NH_3 mass balance



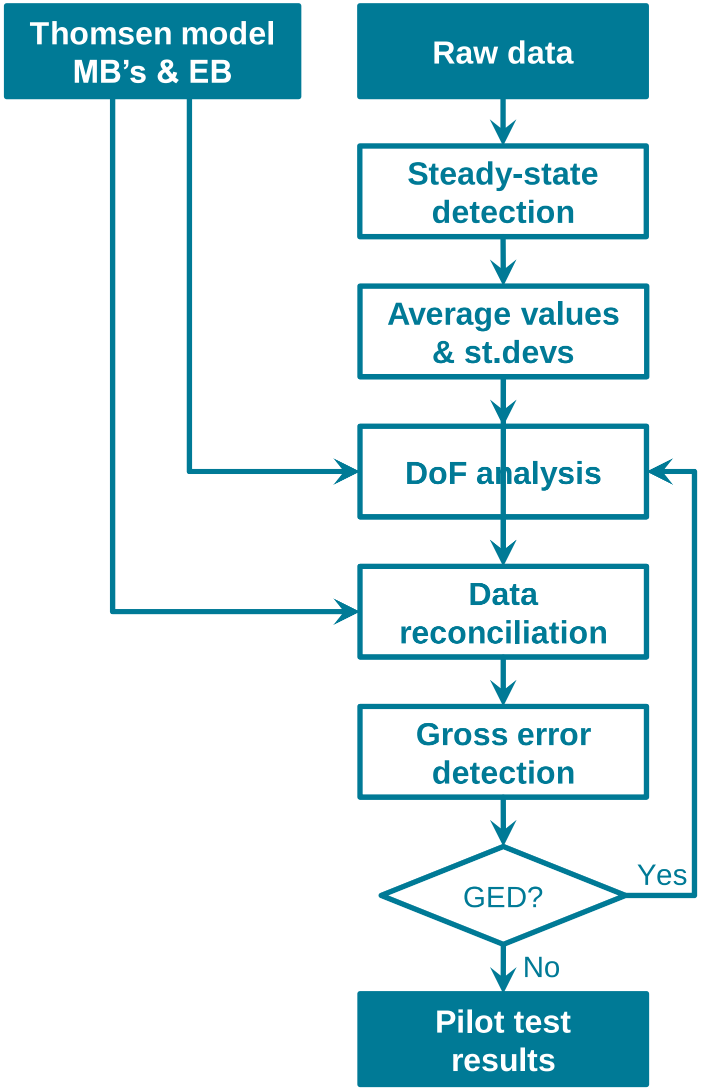
Total mass balance



Energy balance



Systematic treatment of pilot raw data



- **Data reconciliation**[1]

$$F = \min \sum_i \left(\frac{(u_i)_{\mathrm{DR}} - (u_i)_{\mathrm{DM}}}{\sigma_i} \right)^2$$

Reconciled value: $(u_i)_{\mathrm{DR}}$ — Measured value: $(u_i)_{\mathrm{DM}}$

subject to:

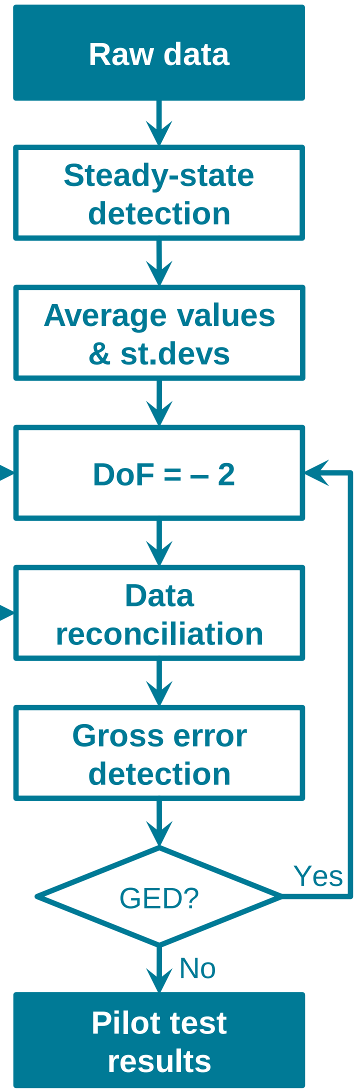
$$\overline{f}(\overline{u_{DR}}, \overline{z}) = 0$$

- CO_2 mass balance
- NH_3 mass balance
- Air mass balance
- Total mass balance
- Energy balance

- **GED**[1] if $e_i = \frac{|(u_i)_{\mathrm{DR}} - (u_i)_{\mathrm{DM}}|}{\sigma_i} \geq e_c$

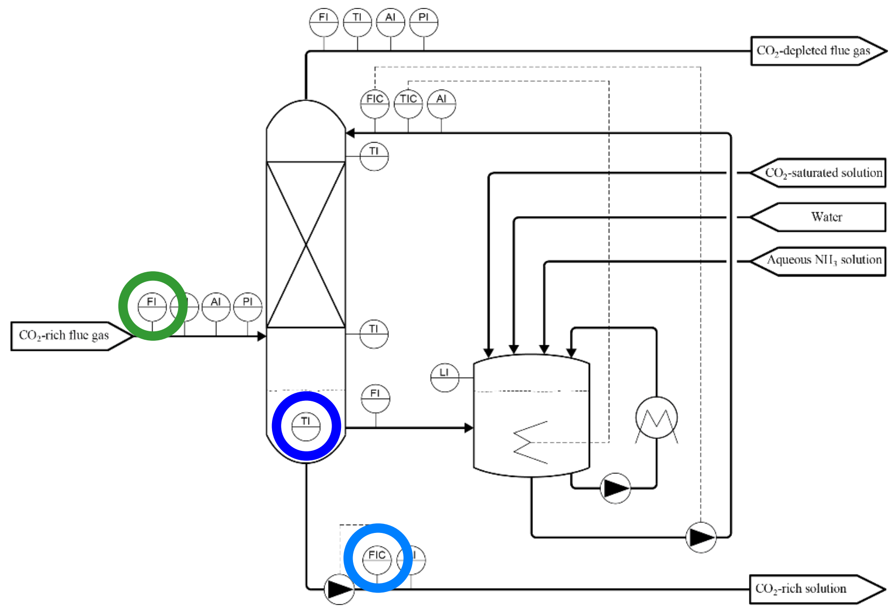
[1] Martínez-Maradiaga et al. *Appl Therm Eng.* 51 (2013) 1170-1180

Systematic treatment of pilot raw data



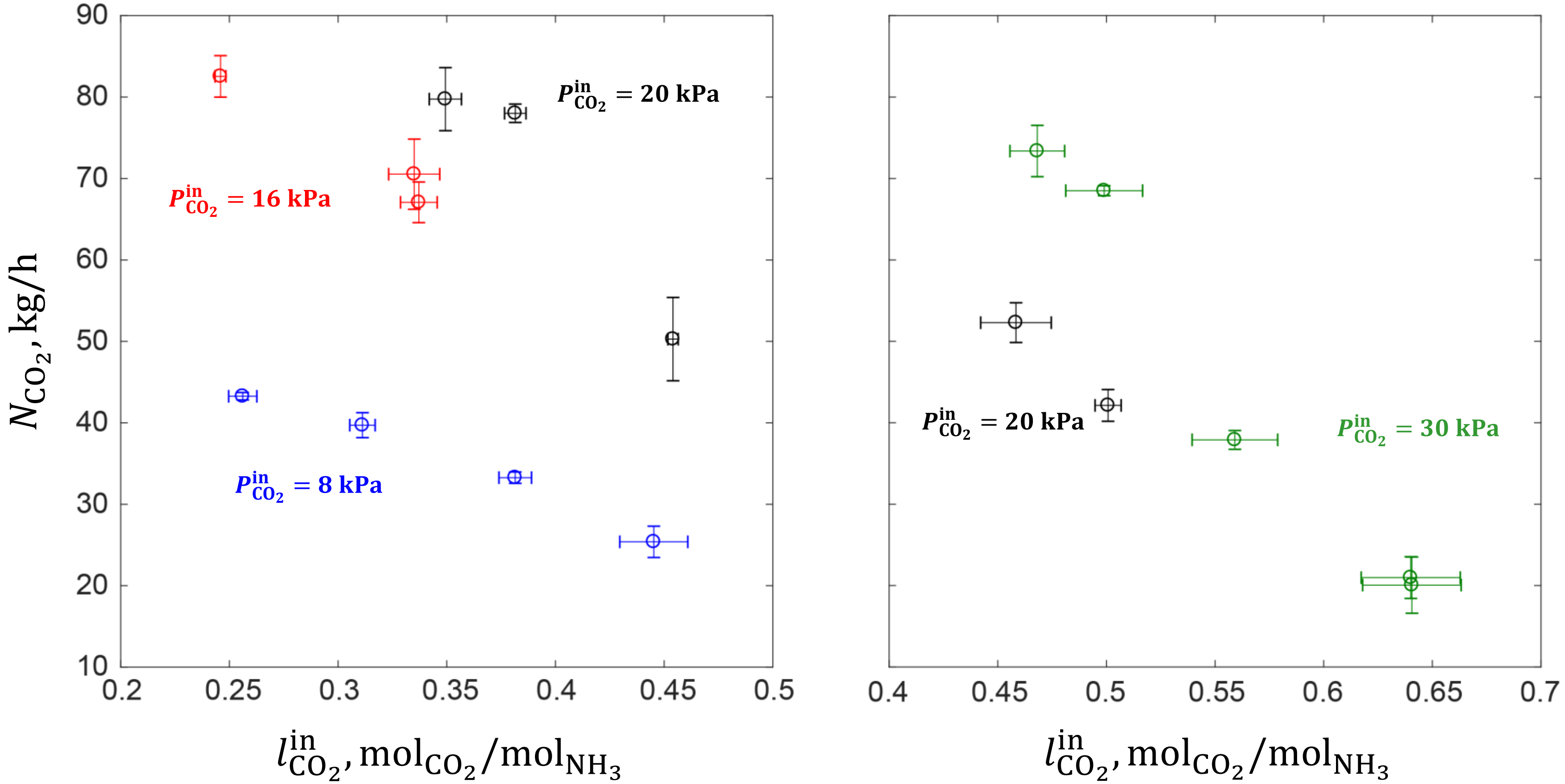
Reconciled ≈ Measured

82 experimental points



- Malfunctioning instruments?
  - Inlet gas flowrate
- Deceptive measurements?
  - Outlet liquid flowrate
  - Outlet liquid temperature
- Unreliable experiments?
  - 7 experimental points discarded

Analysis of pilot test results – CO_2 absorption rate



$m_{NH_3} = 5.7\ mol_{NH_3}/kg_{H_2O}$
$T_L = 16°C$
$\frac{L^{in}}{G^{in}} = 8.7\ kg/kg$
$v^{in}_{s,G} = 1.0\ m/s$

$m_{NH_3} = 6.0\ mol_{NH_3}/kg_{H_2O}$
$T_L = 40°C$
$\frac{L^{in}}{G^{in}} = 11.3\ kg/kg$
$v^{in}_{s,G} = 0.7\ m/s$

Model regression – Carbamate ion reaction kinetics

Pilot plant CO_2 capture tests for cement plant → **Carbamate ion reaction kinetics?** → **Rate-based modelling in Aspen Plus**

Experimental value from pilot tests ← $N_{CO_2} = A_{int} K_{G,CO_2} (P_{CO_2} - P^*_{CO_2})$

$$A_{int} = f\begin{pmatrix}\text{hydrodynamics}\\ \text{transport properties}\end{pmatrix}$$

Rochelle model[1] to compute the **effective G-L interfacial area**

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

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

$$\frac{1}{K_{G,CO_2}} = \frac{RT}{k_{g,CO_2}} + \frac{H_{CO_2}}{E\, k^0_{l,CO_2}}$$

$$\begin{matrix} k_{g,CO_2} \\ k^0_{l,CO_2} \end{matrix} = f\begin{pmatrix}\text{hydrodynamics}\\ \text{transport properties}\end{pmatrix}$$

Rochelle model[1] to compute the **G-film** and **L-film mass-transfer coefficients**

$$H_{CO_2} = f(\text{thermodynamics})$$

Partition coefficient computed by **Thomsen model**

$$E = f(\text{L} - \text{phase reaction kinetics})$$

[1] Wang et al. *Ind Eng Chem Res* 55 (2016) 5357-5384

Model regression – Carbamate ion reaction kinetics

- Tests with $l_{CO_2} < 0.5\ \mathrm{mol}_{CO_2}/\mathrm{mol}_{NH_3}$
- BC formation negligible due to low C_{OH^-}

➔ **Single irreversible reaction**[1,2] ➔ $E = f(\mathrm{Ha})$[3]

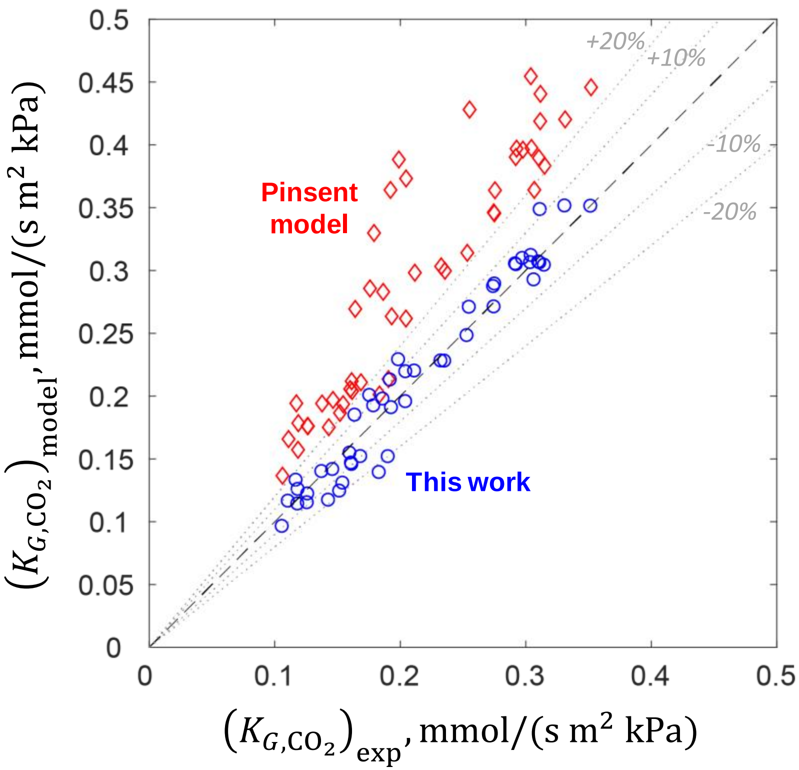
$$CO_2 + 2NH_3 \xrightarrow{k_{cm}} NH_2COO^- + NH_4^+$$

$$\mathrm{Ha} = \frac{\sqrt{k_{cm} C_{NH_3}^{n} D_{CO_2,L}}}{k_{l,CO_2}^{0}}$$

$$r_{cm} = k_{cm} C_{NH_3}^{n} C_{CO_2}$$

$$k_{cm} = k_{0cm,T_{ref}} \exp\left(-\frac{E_{a,cm}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$$

	$k_{cm}(T = T_{ref} = 298\ \mathrm{K})$ $\left[\frac{m^3}{kmol\ s}\right]$	$E_{a,cm}$ $\left[\frac{kJ}{kmol}\right]$	n [–]
This work	190	35300	1.3
Pinsent	431	48500	1



[1] Jilvero et al. Ind Eng Chem Res. 53 (2014) 6750-6758
[2] Ahn et al. *Int J Greenh Gas Control*. 5 (2011) 1606-1613
[3] van Swaaij and Versteeg. *Chem Eng Sci.* 47 (1992) 3181-9195

Conclusions

- The **Chilled Ammonia Process can be applied** for CO_2 capture **to cement plants**
  - The **adaptation** of the **operating conditions in the CO_2 absorber** is required

- CO_2 absorption **pilot tests** have been **performed successfully**, using:
  - Synthetic **flue gases mimicking cement**-like **flue gas** compositions
  - **Liquid compositions and operating conditions** derived **from** the **CAP** heuristic **optimization**, which has been done based on:
    - Assessment of the energy requirements
    - Equilibrium model with ad-hoc Murphree efficiencies for cement plant flue gas compositions

- A **kinetic model** for the **formation of the carbamate ion** has been **regressed** in order to be used with engineering purposes

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