



Development of an ammonia-based process for CO₂ capture in cement plants: absorption tests, rate-based modelling and process optimization

José-Francisco Pérez-Calvo, Daniel Sutter, Federico Milella, Matteo Gazzani, Marco Mazzotti
Institute of Process Engineering, ETH Zurich

PCCC4, 5th – 8th September, 2017

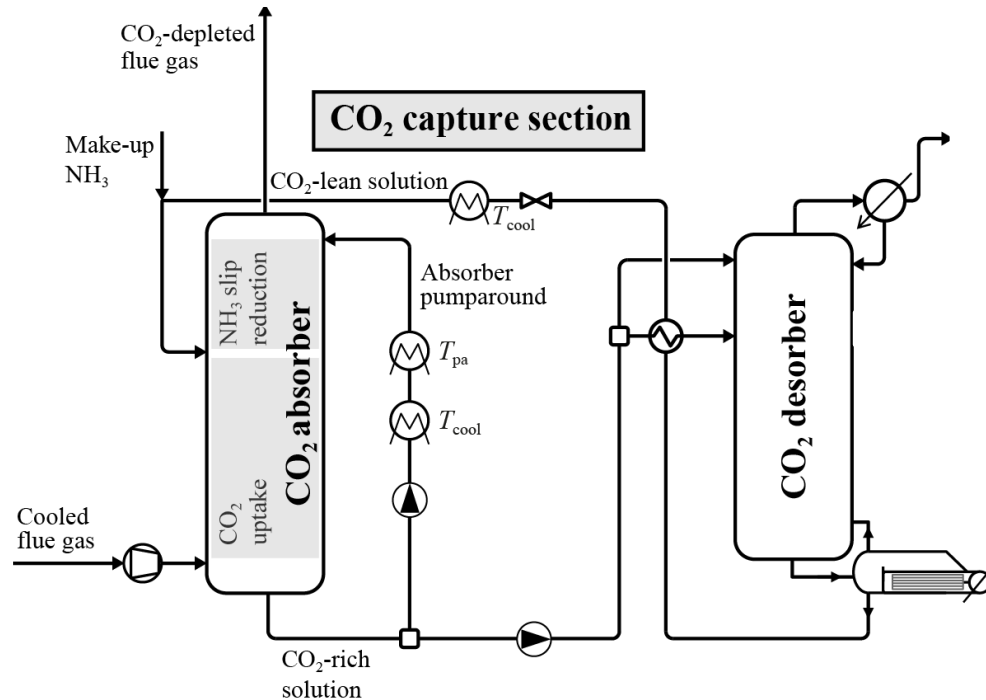
Talk outline

- **Introduction and scope** of the study
- **Model**
- **CAP heuristic optimization for cement plants**
- **Pilot plant tests** of the CO₂ absorber
- **Regression of kinetic parameters**
- **Conclusions**

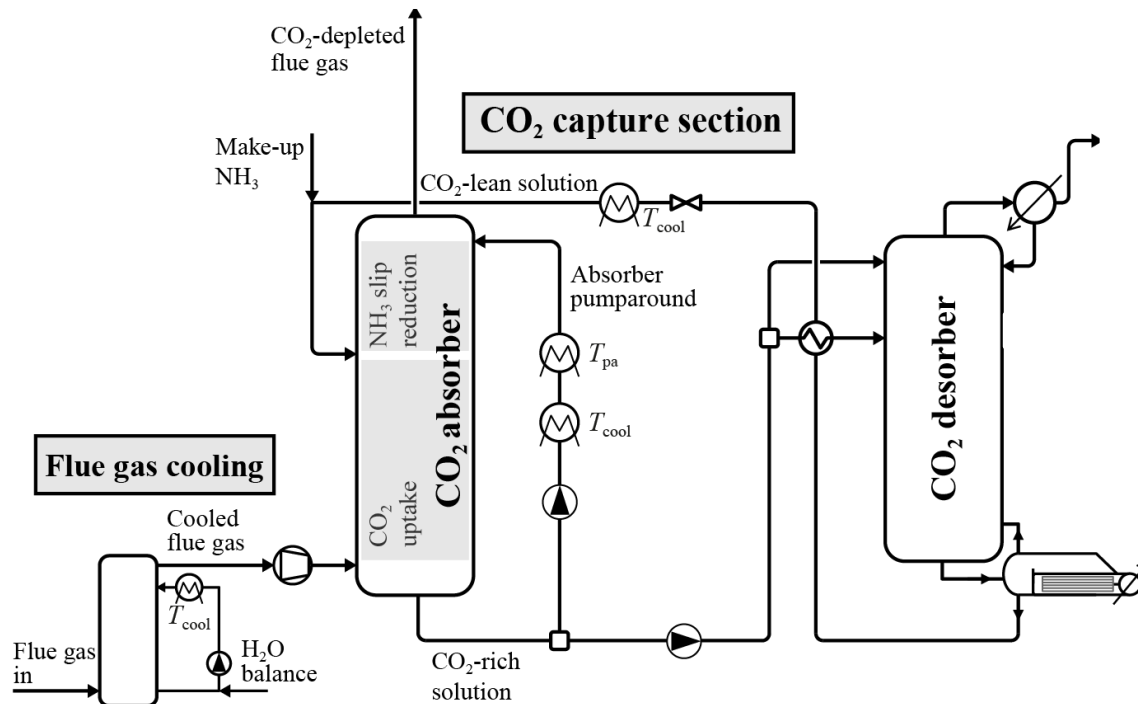
CO₂ emissions from cement & the CAP

- 5% of global anthropogenic CO₂ emissions
- ~ 0.58 t CO₂/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

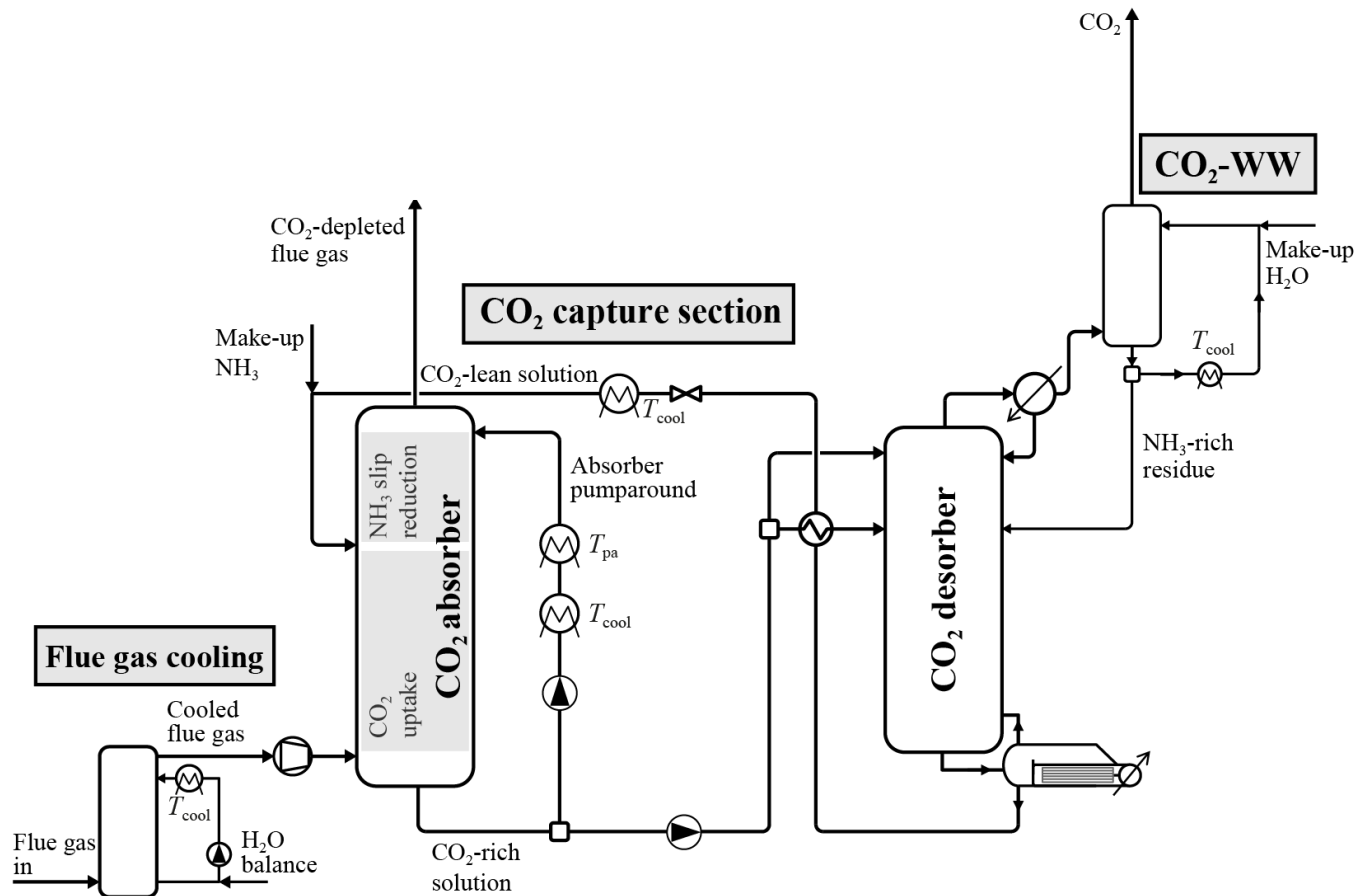
The Chilled Ammonia Process



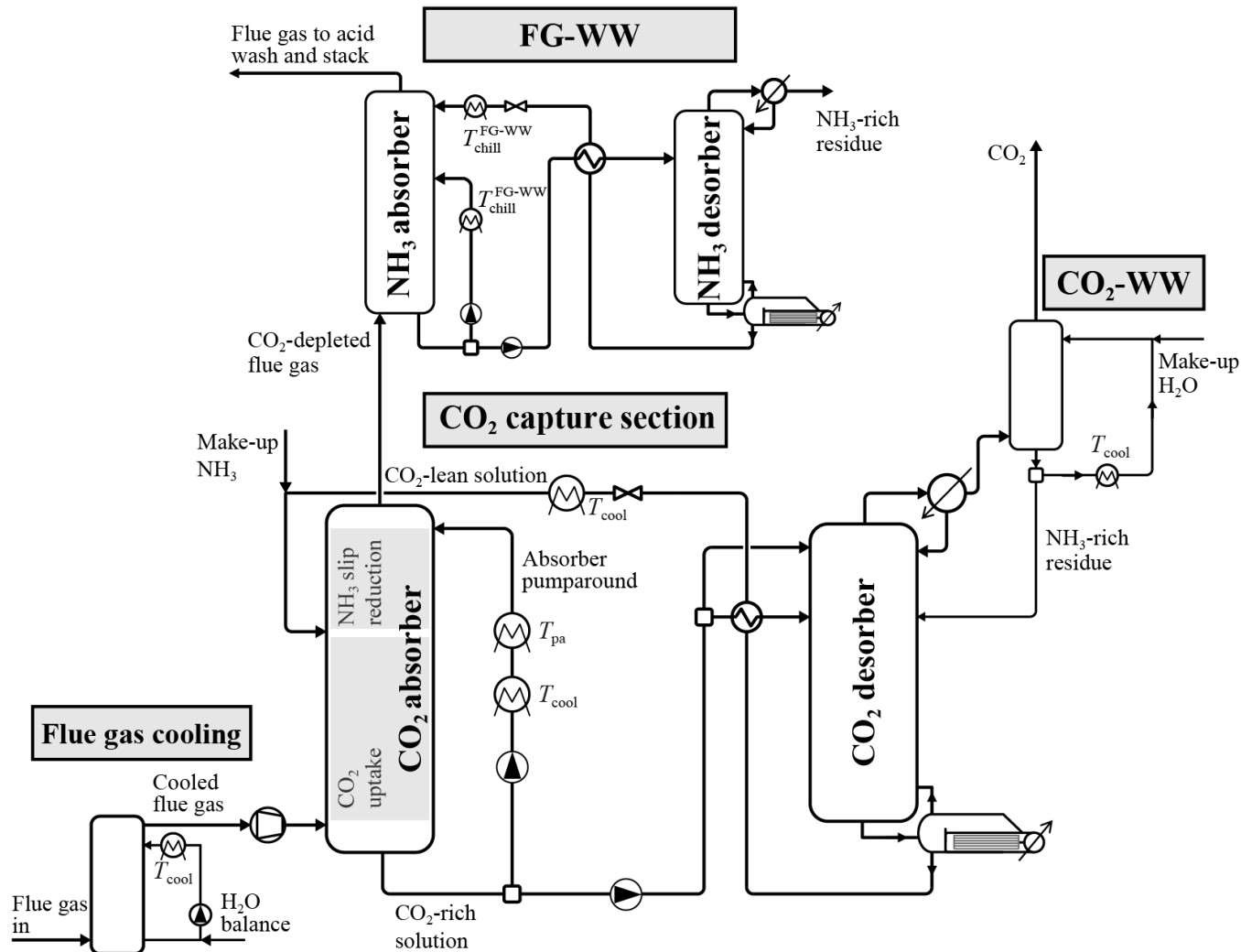
The Chilled Ammonia Process



The Chilled Ammonia Process



The Chilled Ammonia Process

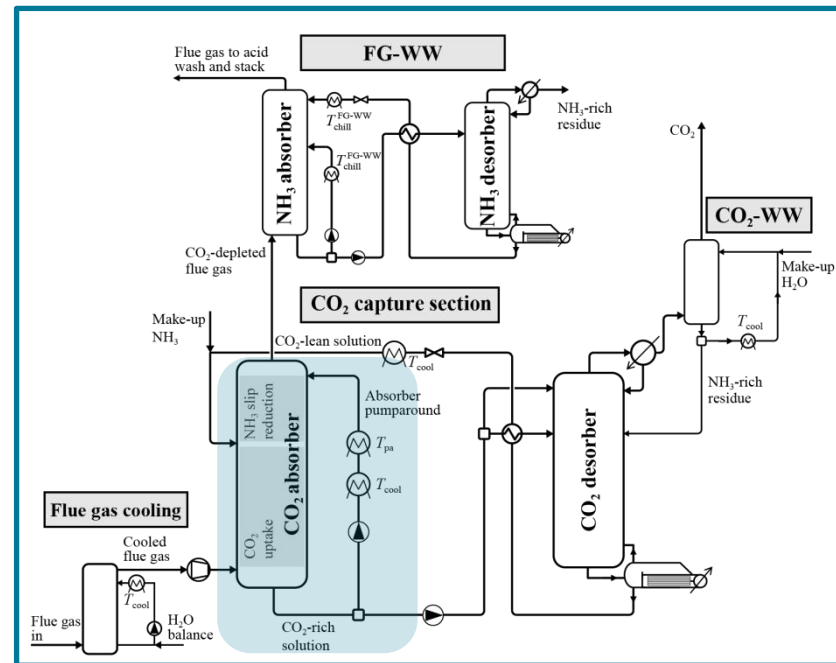


From power plants to cement plants

NG power plants
~ 4 %vol. CO₂

Coal-fired power plants
~ 14 %vol. CO₂

Cement plants
15 – 35%vol. CO₂



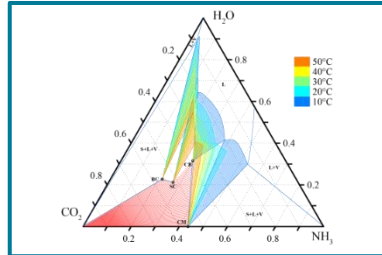
Adaptation of
operating conditions

Model-based optimization

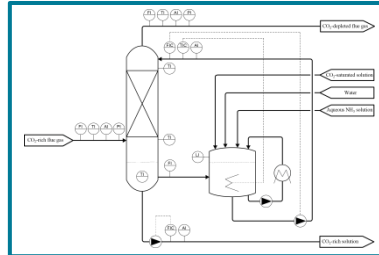
- Process complexity
- Heat integration
- Thermodynamics
- Kinetics

Scope of the study

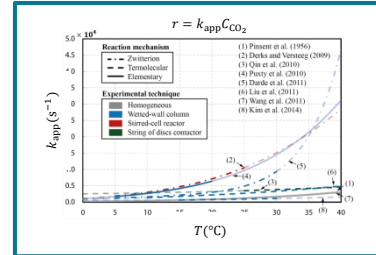
Equilibrium model (Aspen Plus)



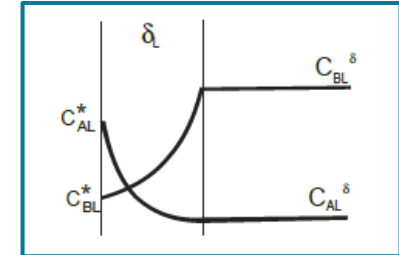
Pilot plant tests



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

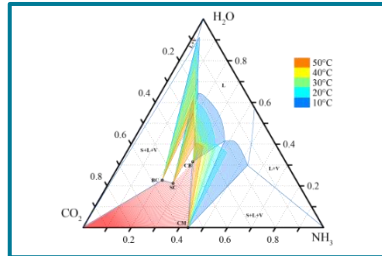
[2] Darde et al. *Ind Eng Chem Res* 49 (2010) 12663-74

[3] Sutter et al. *Faraday Discuss* 192 (2016) 59-83

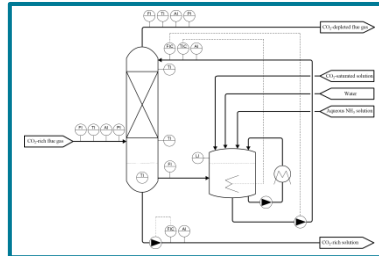
[4] Jilvero et al. *Ind Eng Chem Res* 53 (2014) 6750-6758

Scope of the study

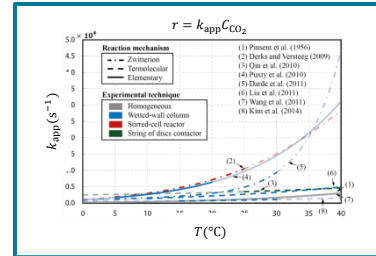
Equilibrium model (Aspen Plus)



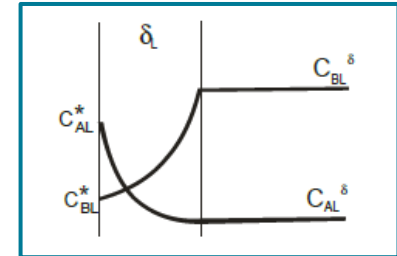
Pilot plant tests



Reaction kinetics



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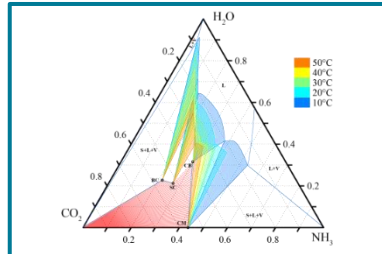
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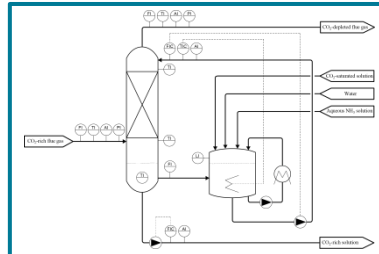
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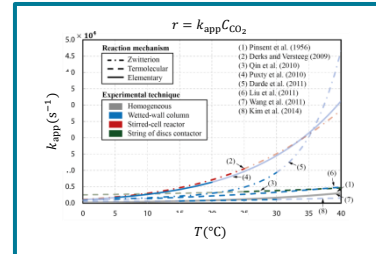
Equilibrium model (Aspen Plus)



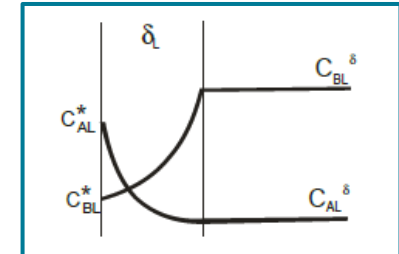
Pilot plant tests



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]

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

5

Model-based optimization

Model-based optimization

[1] Thomsen and Rasmussen *Chem Eng Sci* 54 (1999) 1787-1802

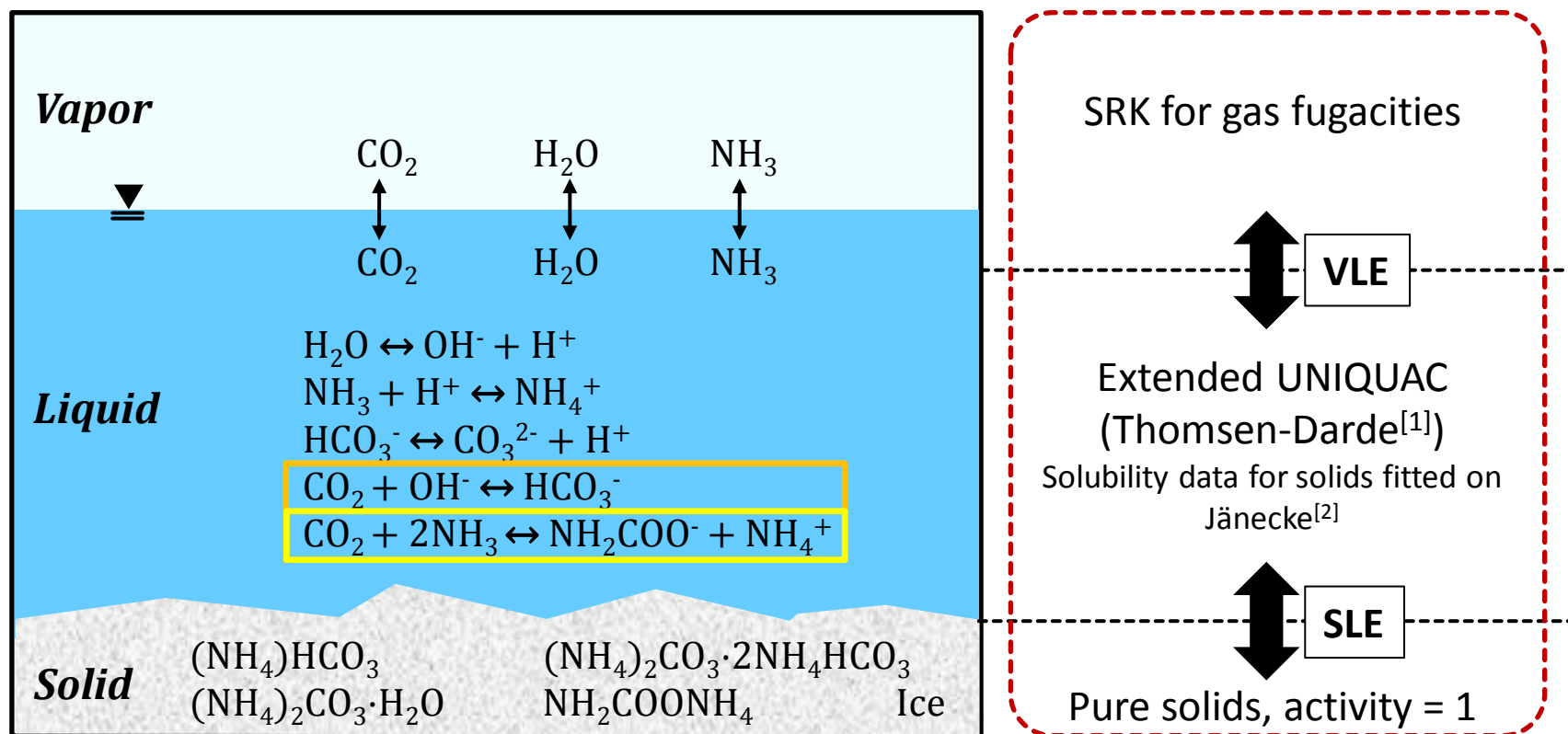
[2] Darde et al. *Ind Eng Chem Res* 49 (2010) 12663-74

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Thermodynamic model: CO₂-NH₃-H₂O system

Thomsen model to predict the system thermodynamics

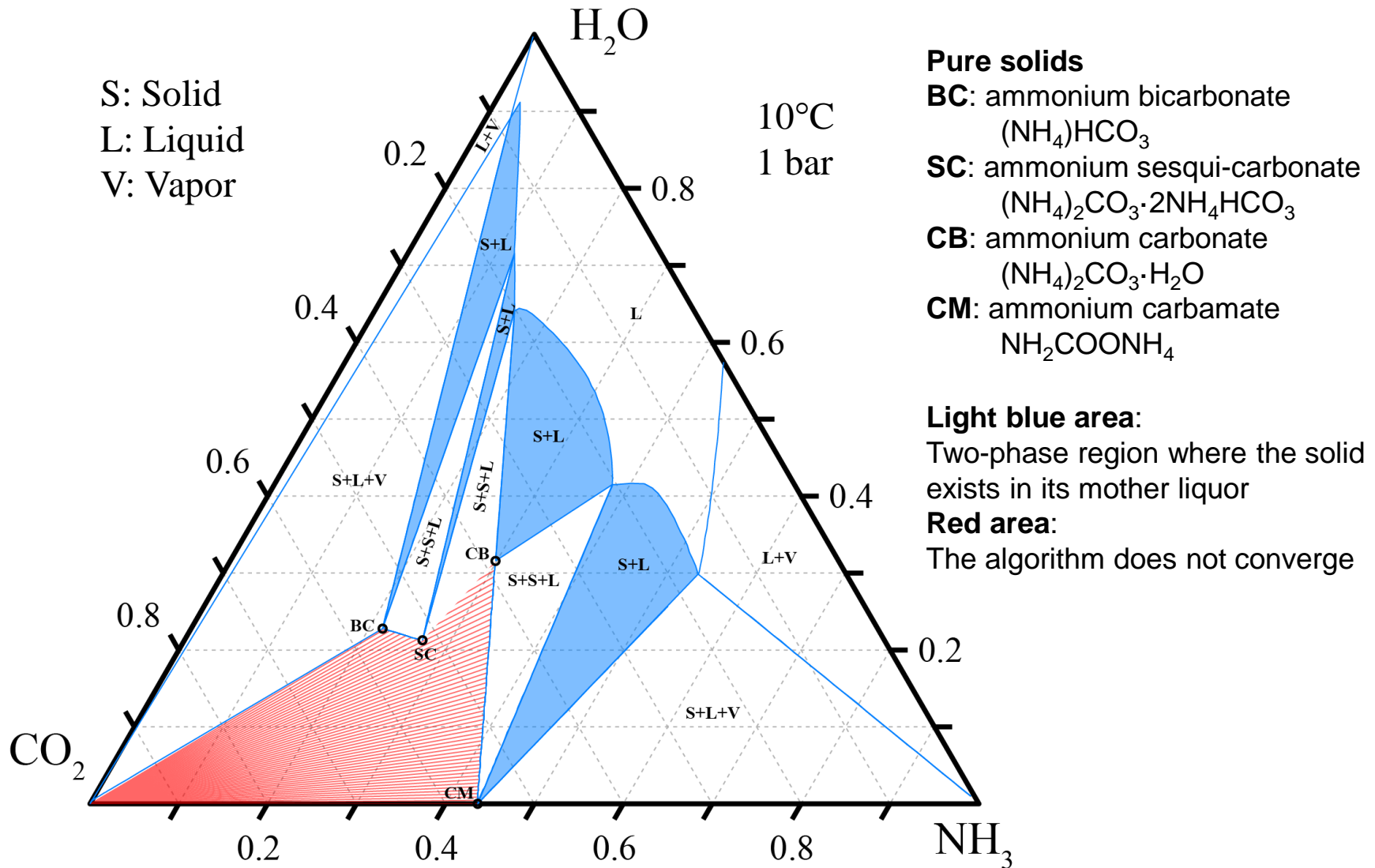


[1] Darde et al. *Ind Eng Chem Res* 49 (2010) 12663-74

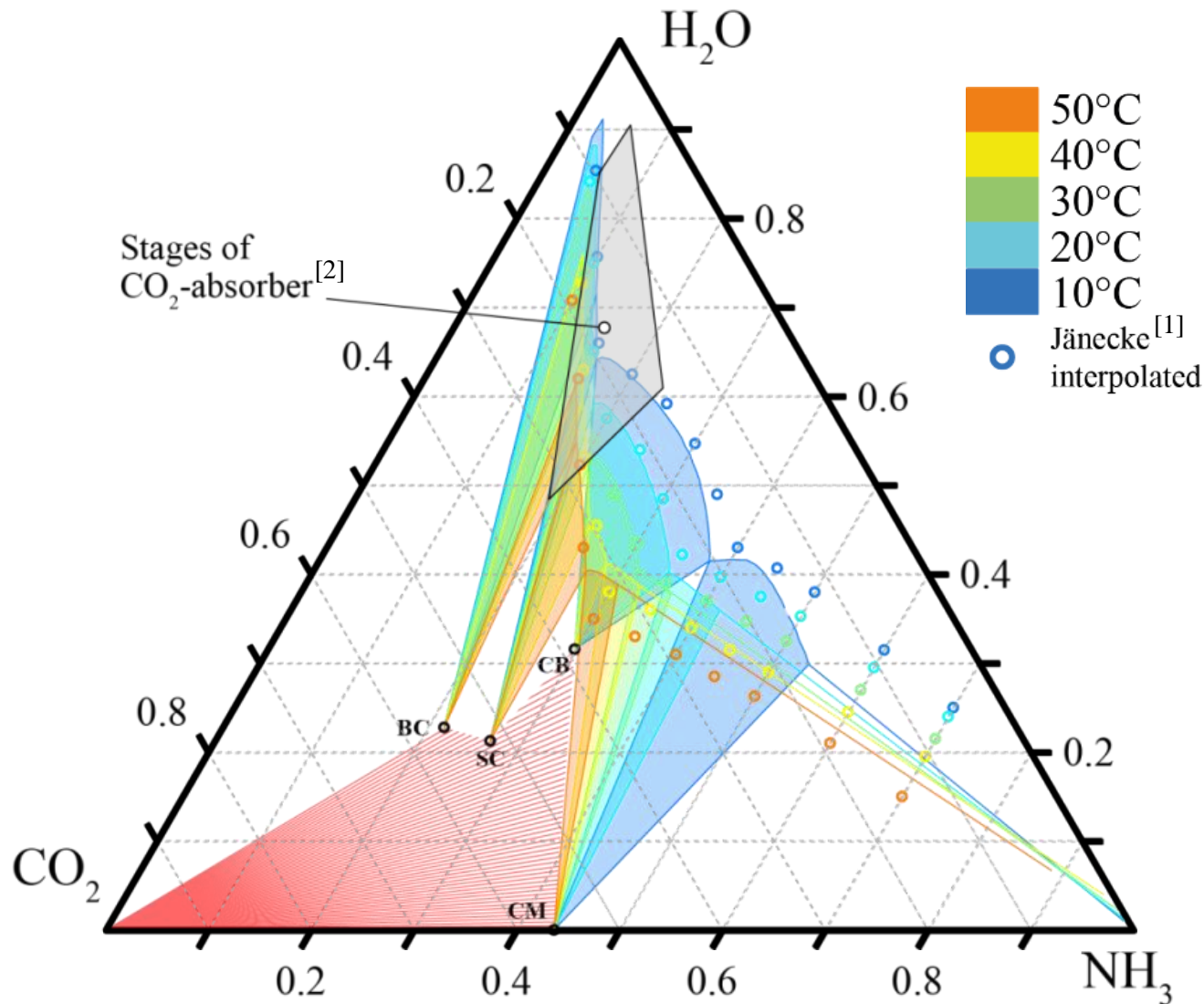
[2] Jänecke *Z Elektrochem* 35 (1929) 9:716-28

External routine in Aspen
from Thomsen group

Phase diagram: CO₂-NH₃-H₂O system



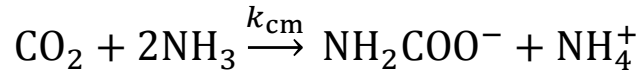
Phase diagram: CO₂-NH₃-H₂O system



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

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

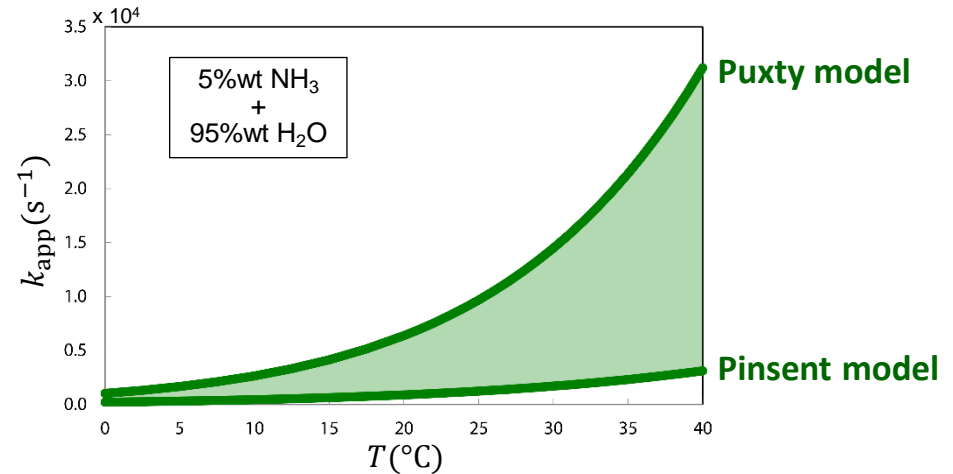
Rate-based model validation with CSIRO tests



$$r_{\text{cm}} = k_{\text{app}} C_{\text{CO}_2}$$

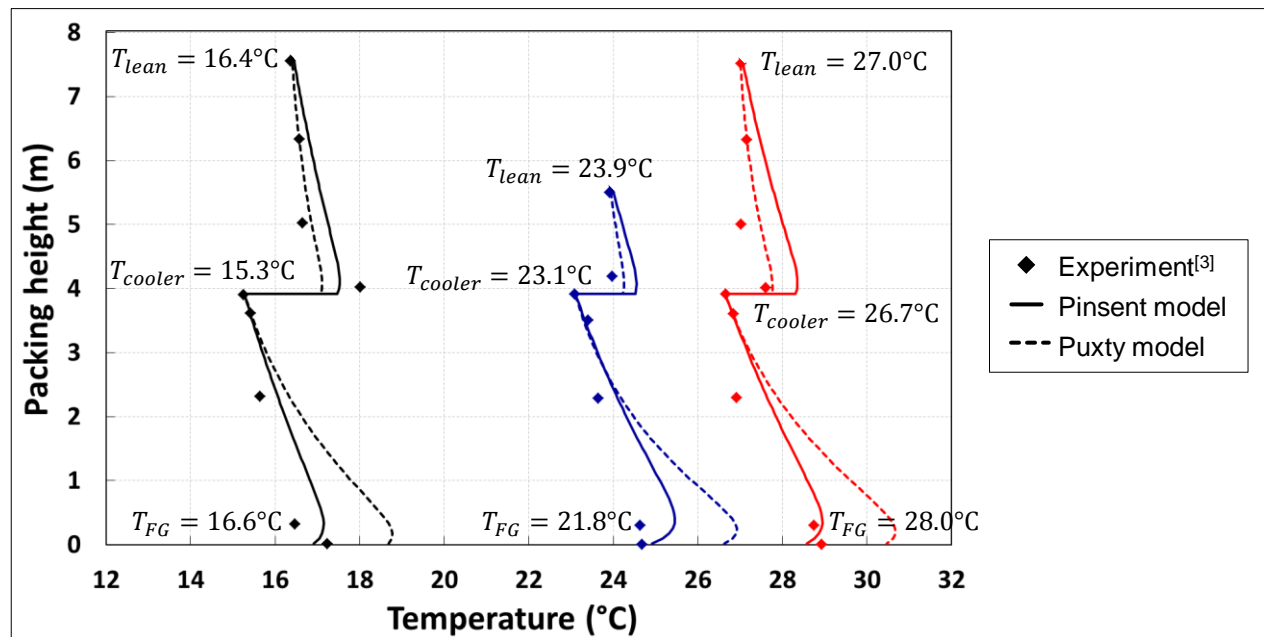
[1] Pinsent et al. *Trans Faraday Soc.* 52 (1956) 1594-1598

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



Rate-based model with:

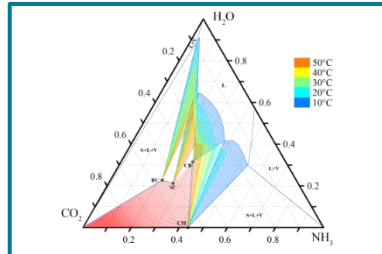
- Thomsen model
- Reaction kinetics:
 - Pinsent model
 - Puxty model



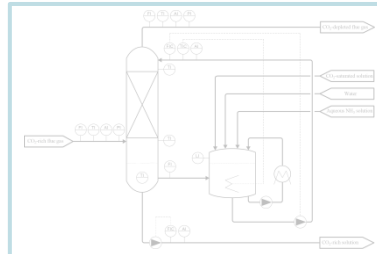
[3] Qi et al. *Int J Greenh Gas Con* 17 (2013) 450-461

From the power plant to the cement plant

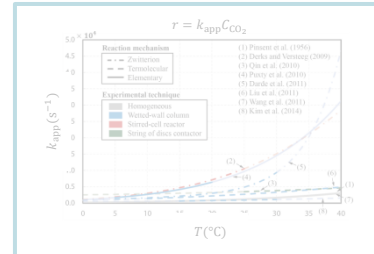
Equilibrium model (Aspen Plus)



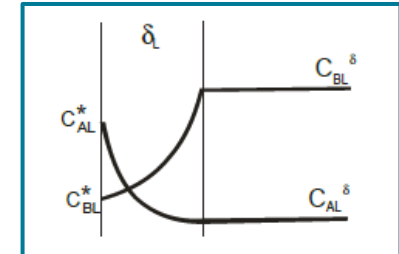
Pilot plant tests



Reaction kinetics



Rate-based model (Aspen Plus)



Power plant

Starting point

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

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- Model validation with CSIRO pilot tests

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- Literature research

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- Thomsen model
- Pinsent model

Cement plant

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- Ad-hoc Murphree efficiencies for cement plants
- Thomsen model

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

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- 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

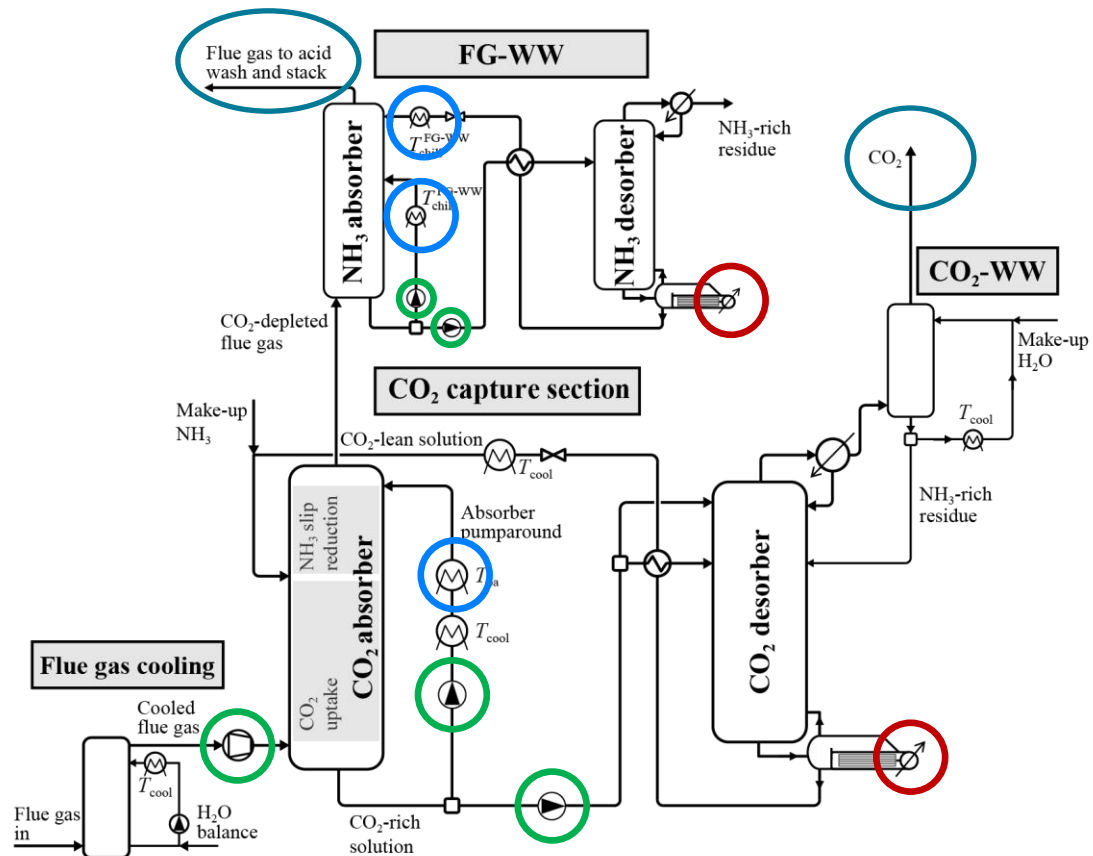
$$W = \frac{W_{\text{reboilers}} + W_{\text{chilling}} + W_{\text{auxiliaries}}}{m_{\text{CO}_2}^{\text{abs}}} \left[\frac{\text{MJ}}{\text{kg CO}_2 \text{ captured}} \right]$$

Operating conditions varied in the CO₂ absorber

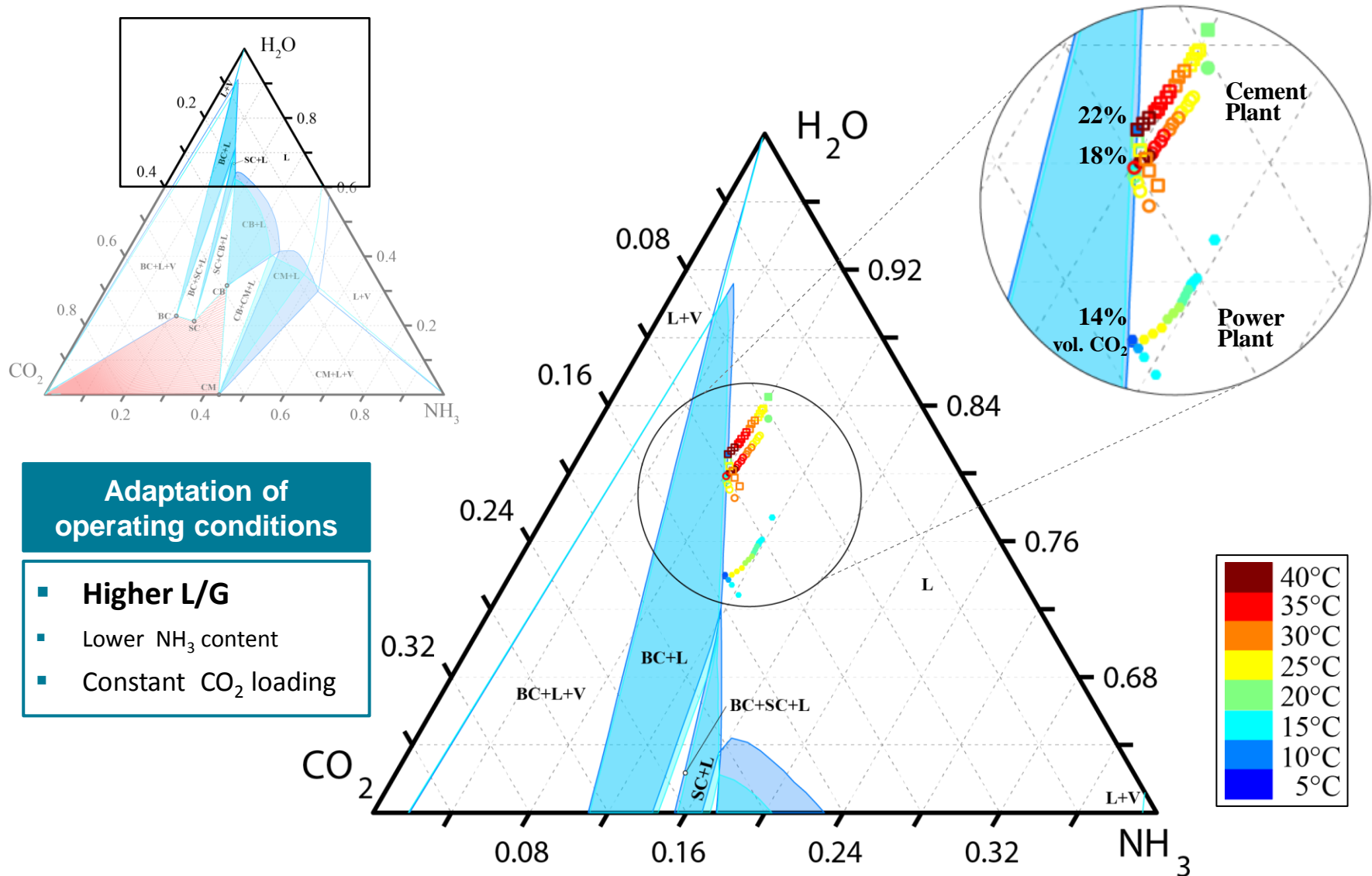
- L/G
- CO₂ loading
- NH₃ concentration
- Pumparound:
 - Temperature
 - Split fraction

Specifications and constraints

- CO₂ capture > 85 %
- CO₂ purity > 99 %mole
- NH₃ slip < 200 ppm
- No solid formation



CO₂ absorber profiles for optimum operating conditions



Definition of the test matrix for new absorber pilot tests

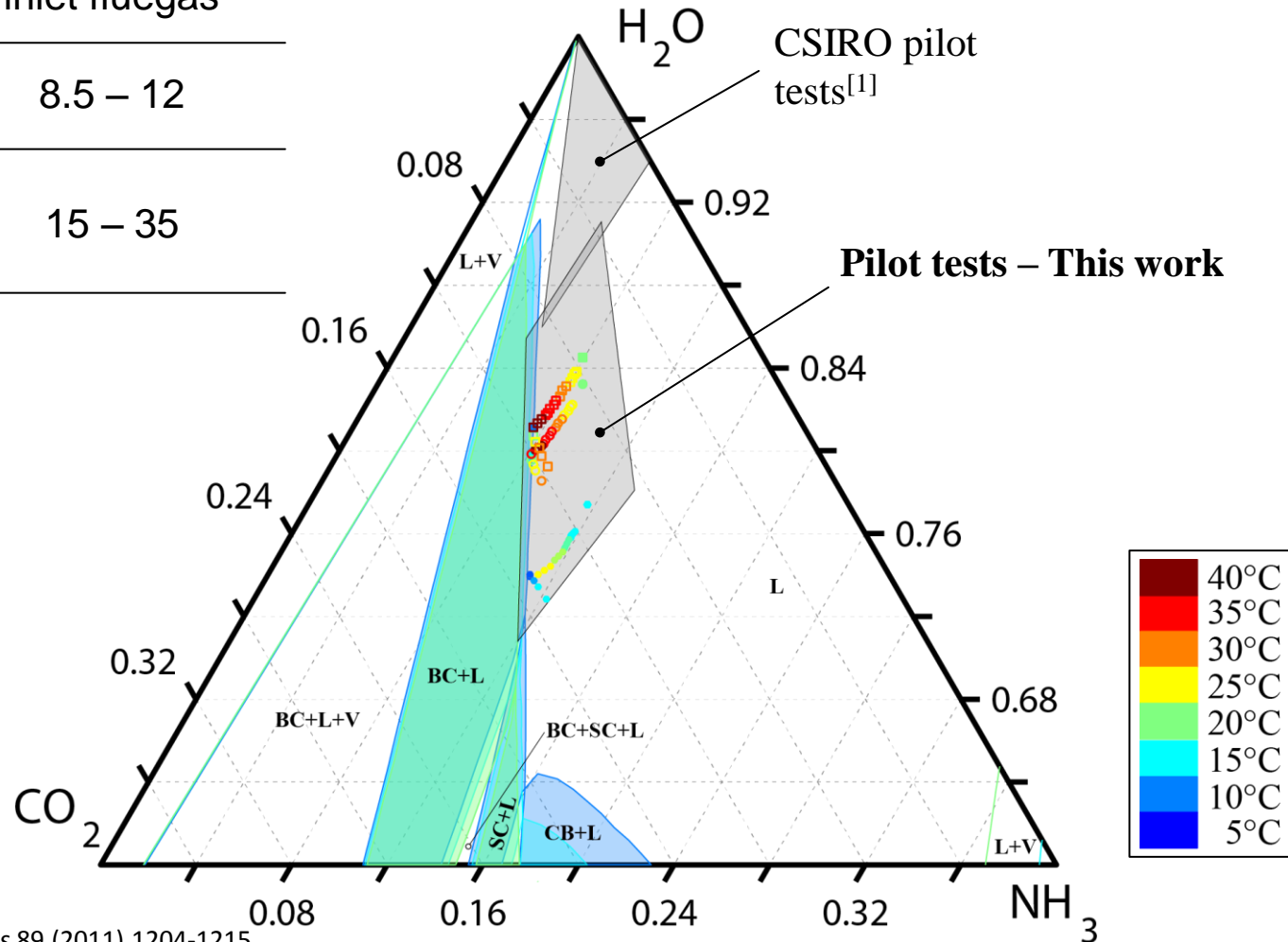
%vol CO₂ in the inlet fluegas

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

$$l_{\text{CO}_2}^{\text{in}} = 0.25 - 0.70 \text{ mol}_{\text{CO}_2} / \text{mol}_{\text{NH}_3}$$

$$m_{\text{NH}_3}^{\text{in}} = 3.5 - 10.0 \text{ mol}_{\text{NH}_3} / \text{kg}_{\text{H}_2\text{O}}$$

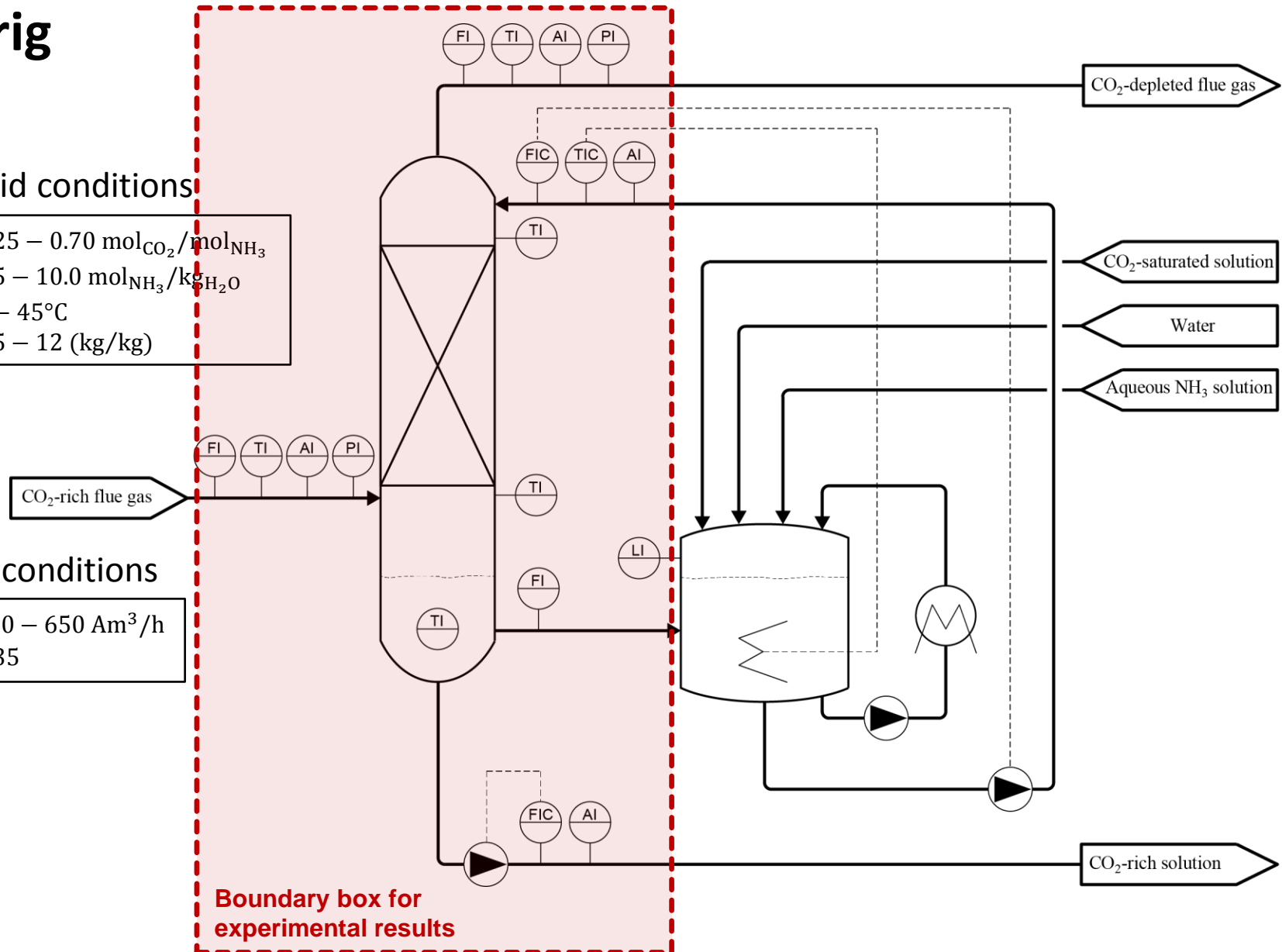
$$T_L^{\text{in}} = 5 - 45^\circ\text{C}$$

$$L/G = 2.5 - 12 \text{ (kg/kg)}$$

Inlet gas conditions

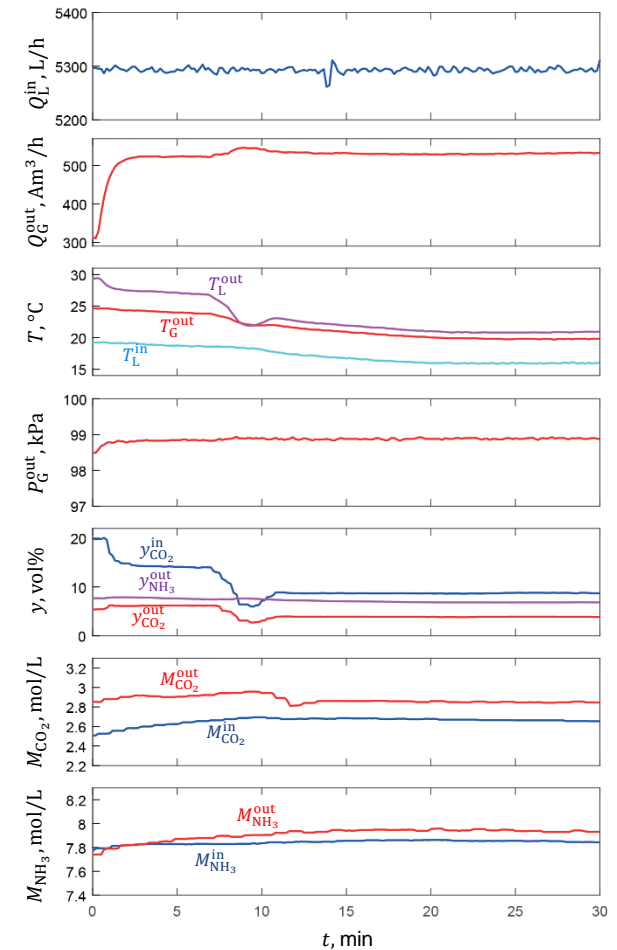
$$Q_G^{\text{in}} = 400 - 650 \text{ Am}^3/\text{h}$$

$$y_{\text{CO}_2}^{\text{in}} \leq 0.35$$



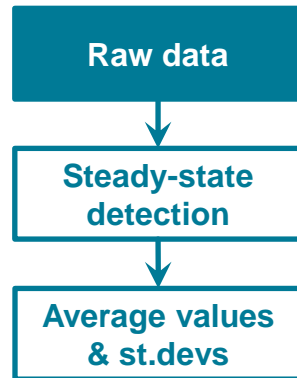
Systematic treatment of pilot raw data

Raw data

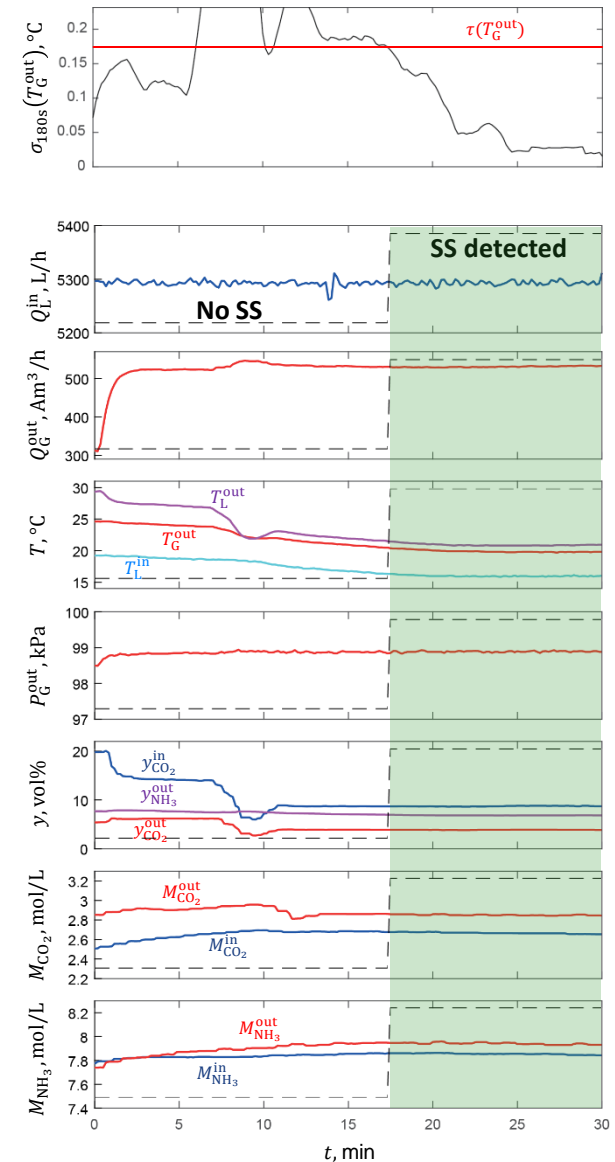


[1] Martínez-Maradiaga et al. *Appl Therm Eng.* 51 (2013) 1170-1180

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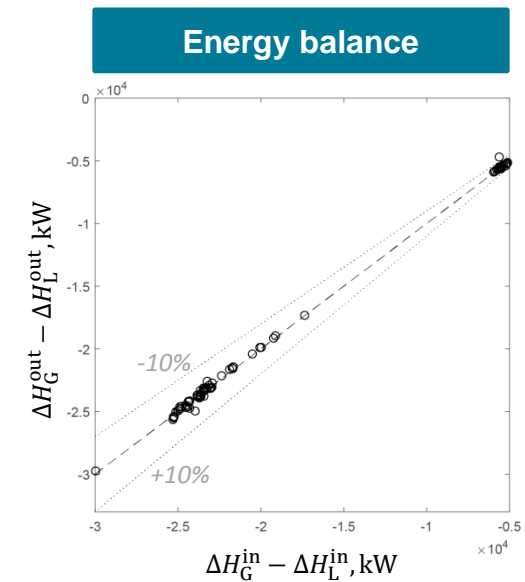
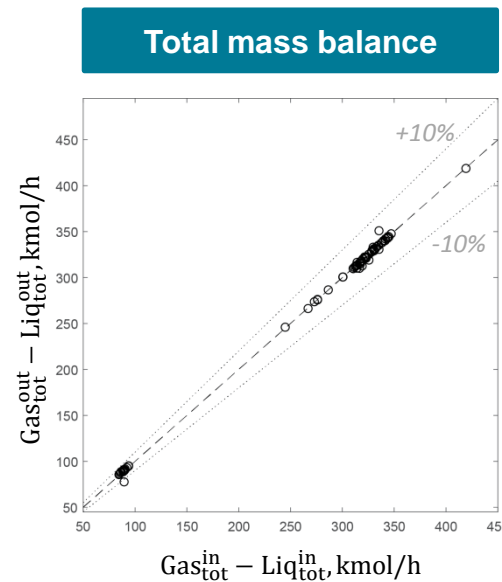
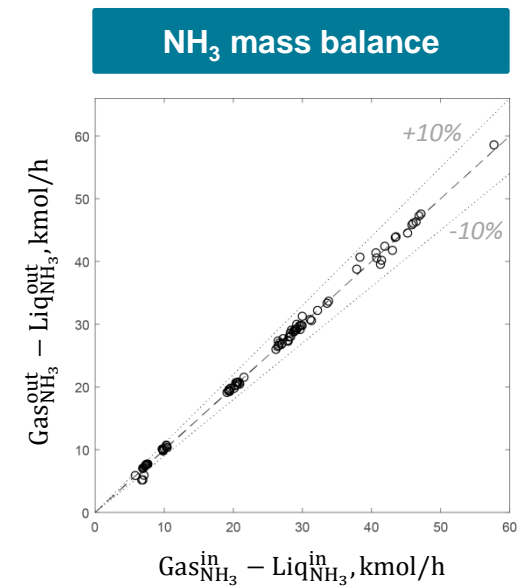
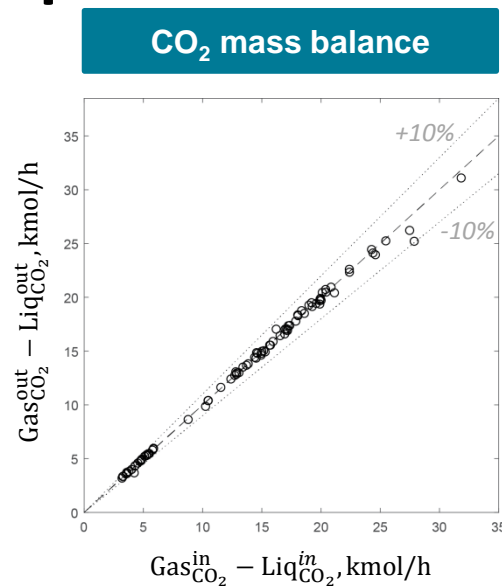
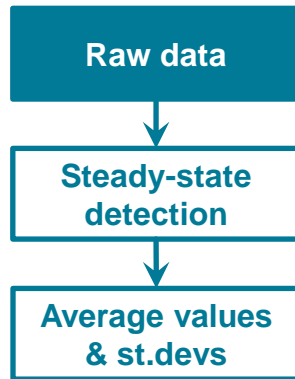


- Methodology based on a moving window^[1]

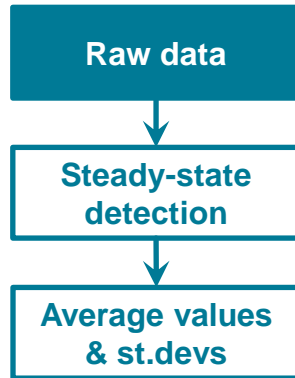


[1] Kim et al. *Int J Refrig.* 31 (2008) 790-799

Systematic treatment of pilot raw data



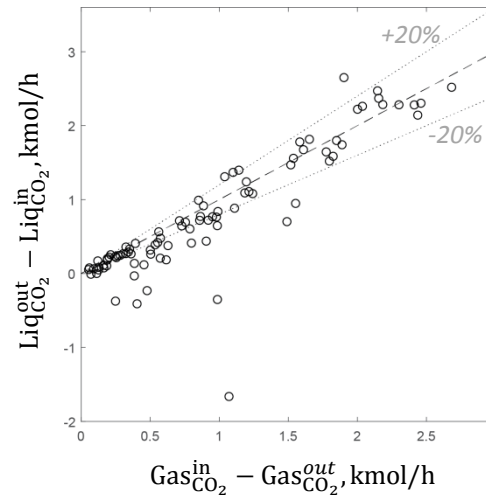
Systematic treatment of pilot raw data



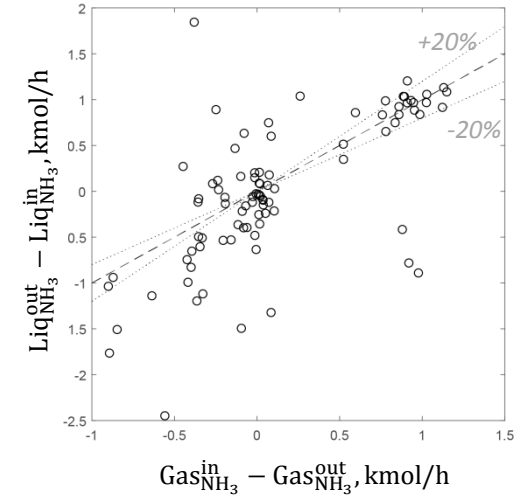
- Malfunctioning instruments?
- Deceptive measurements?
- Unreliable experiments?

Which experiments and measurements can we trust?

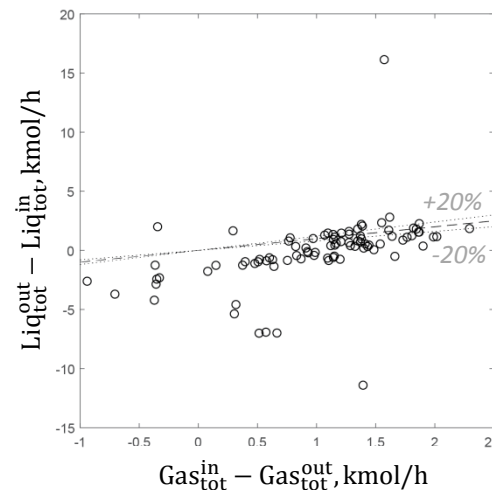
CO₂ mass balance



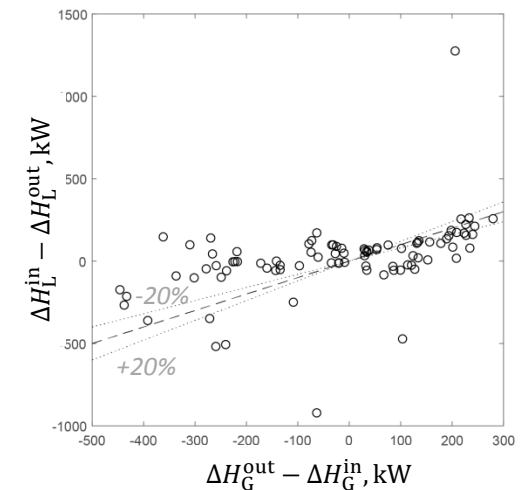
NH₃ mass balance



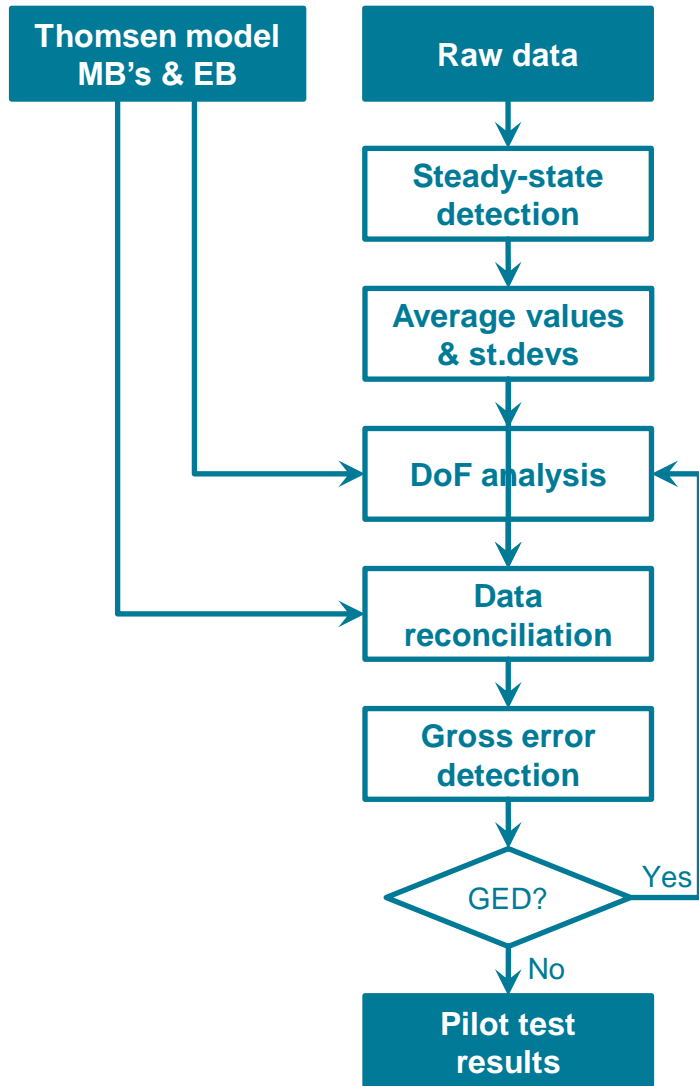
Total mass balance



Energy balance



Systematic treatment of pilot raw data



Data reconciliation^[1]

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

Reconciled value Measured value

subject to:

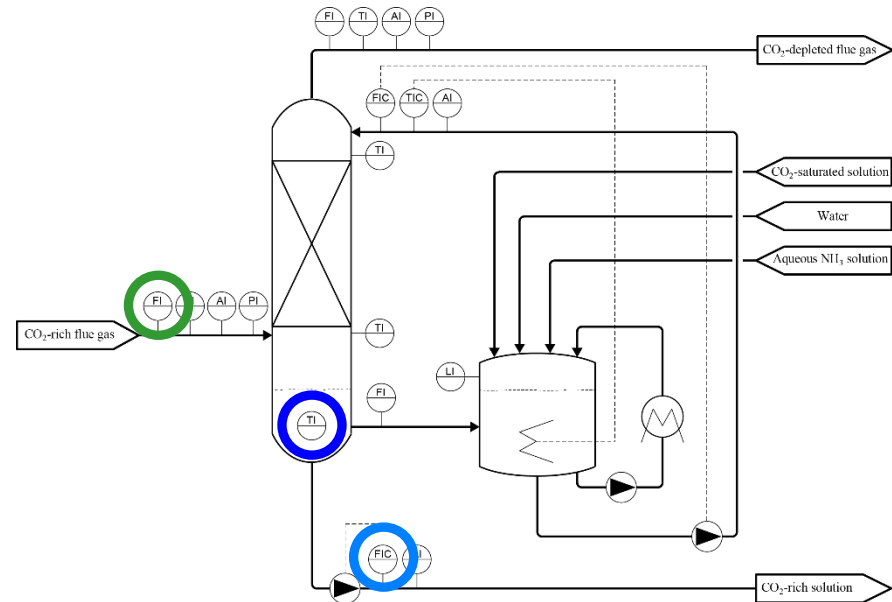
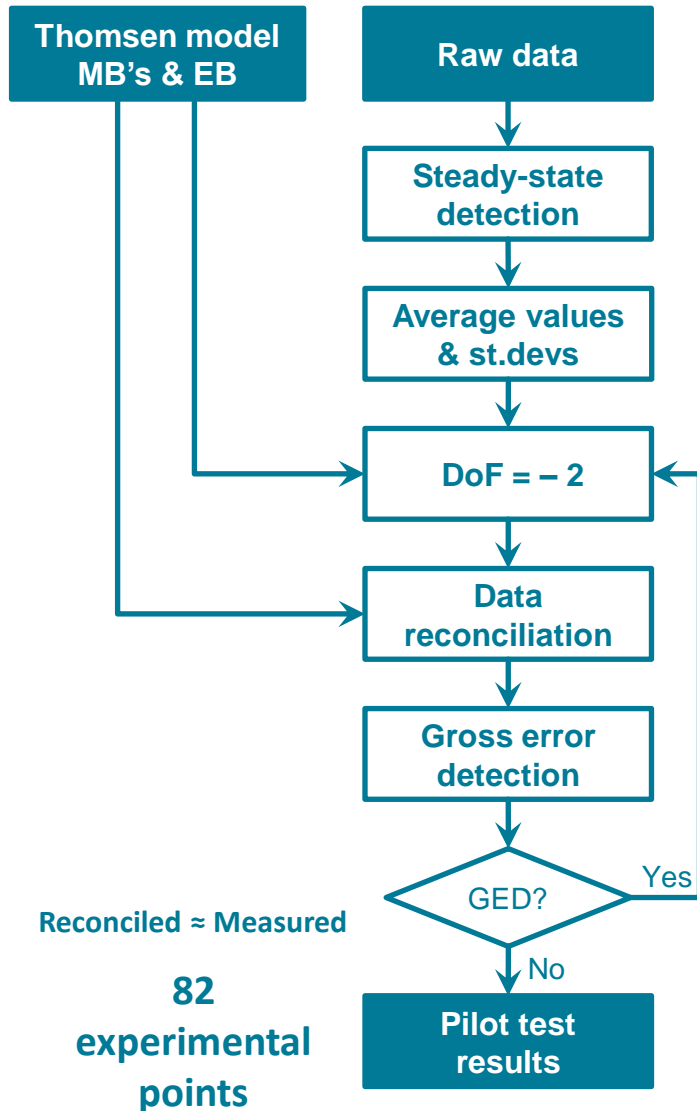
$$\bar{f}(\bar{u}_{DR}, \bar{z}) = 0$$

- CO₂ mass balance
- NH₃ mass balance
- Air mass balance
- Total mass balance
- Energy balance

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

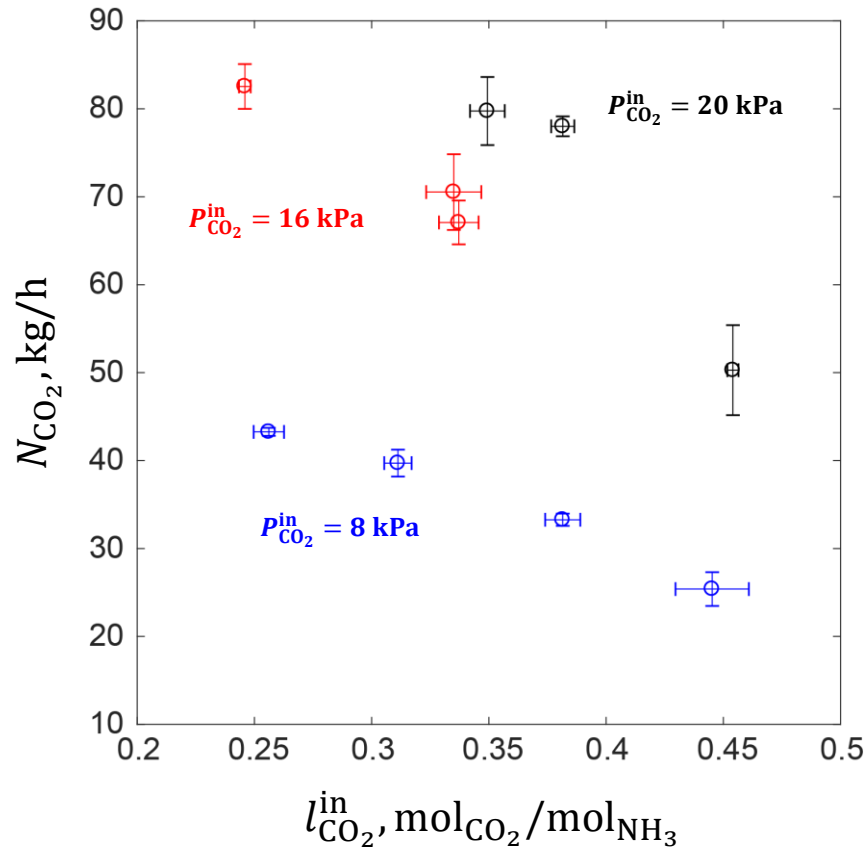
[1] Martínez-Maradiaga et al. *Appl Therm Eng.* 51 (2013) 1170-1180

Systematic treatment of pilot raw data

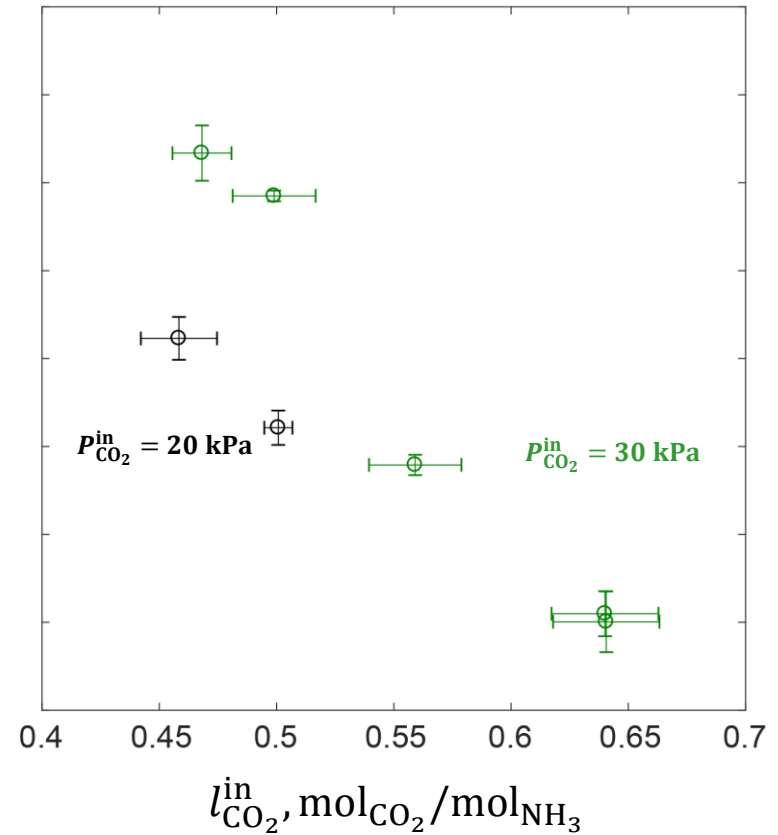


- Malfunctioning instruments?
Inlet gas flowrate
- Deceptive measurements?
Outlet liquid flowrate
Outlet liquid temperature
- Unreliable experiments?
7 experimental points discarded

Analysis of pilot test results – CO₂ absorption rate



$$\begin{aligned}
 m_{\text{NH}_3} &= 5.7 \text{ mol}_{\text{NH}_3}/\text{kg}_{\text{H}_2\text{O}} \\
 T_L &= 16^\circ\text{C} \\
 \frac{L^{\text{in}}}{G^{\text{in}}} &= 8.7 \text{ kg/kg} \\
 v_{S,G}^{\text{in}} &= 1.0 \text{ m/s}
 \end{aligned}$$



$$\begin{aligned}
 m_{\text{NH}_3} &= 6.0 \text{ mol}_{\text{NH}_3}/\text{kg}_{\text{H}_2\text{O}} \\
 T_L &= 40^\circ\text{C} \\
 \frac{L^{\text{in}}}{G^{\text{in}}} &= 11.3 \text{ kg/kg} \\
 v_{S,G}^{\text{in}} &= 0.7 \text{ m/s}
 \end{aligned}$$

Model regression – Carbamate ion reaction kinetics

Pilot plant CO₂ capture tests for cement plant

Carbamate ion reaction kinetics?

Rate-based modelling in Aspen Plus

Experimental value from pilot tests

$$N_{\text{CO}_2} = A_{\text{int}} K_{\text{G,CO}_2} (P_{\text{CO}_2} - P_{\text{CO}_2}^*)$$

$$A_{\text{int}} = f \left(\begin{array}{l} \text{hydrodynamics} \\ \text{transport properties} \end{array} \right)$$

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

$$(P_{\text{CO}_2} - P_{\text{CO}_2}^*) = f(\text{thermodynamics})$$

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

$$\frac{1}{K_{\text{G,CO}_2}} = \frac{RT}{k_{\text{g,CO}_2}} + \frac{H_{\text{CO}_2}}{E k_{\text{l,CO}_2}^0}$$

$$k_{\text{g,CO}_2} = f \left(\begin{array}{l} \text{hydrodynamics} \\ \text{transport properties} \end{array} \right)$$

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

$$H_{\text{CO}_2} = f(\text{thermodynamics})$$

Partition coefficient computed by Thomsen model

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

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

Model regression – Carbamate ion reaction kinetics

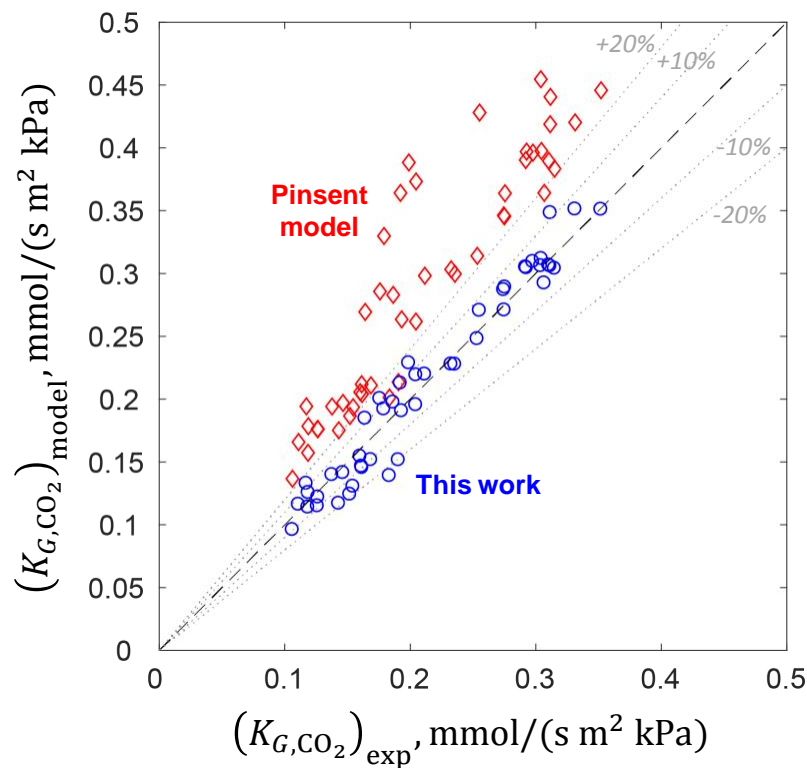
- Tests with $l_{\text{CO}_2} < 0.5 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{NH}_3}$
 - BC formation negligible due to low C_{OH^-}
- Single irreversible reaction^[1,2] → $E = f(\text{Ha})^{[3]}$
- $$\text{CO}_2 + 2\text{NH}_3 \xrightarrow{k_{\text{cm}}} \text{NH}_2\text{COO}^- + \text{NH}_4^+$$

$$\text{Ha} = \sqrt{\frac{k_{\text{cm}} C_{\text{NH}_3}^n D_{\text{CO}_2, \text{L}}}{k_{l, \text{CO}_2}^0}}$$

$$r_{\text{cm}} = k_{\text{cm}} C_{\text{NH}_3}^n C_{\text{CO}_2}$$

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

	$k_{\text{cm}}(T = T_{\text{ref}} = 298 \text{ K})$	$E_{a, \text{cm}}$	n
	$\left[\frac{\text{m}^3}{\text{kmol s}}\right]$	$\left[\frac{\text{kJ}}{\text{kmol}}\right]$	$[-]$
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 CO₂ capture **to cement plants**
 - The **adaptation of the operating conditions in the CO₂ absorber** is required
- CO₂ 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

Acknowledgements

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