# Pilot Tests and Rate-Based Modelling of $CO_2$ Capture in Cement Plants Using an Aqueous Ammonia Solution

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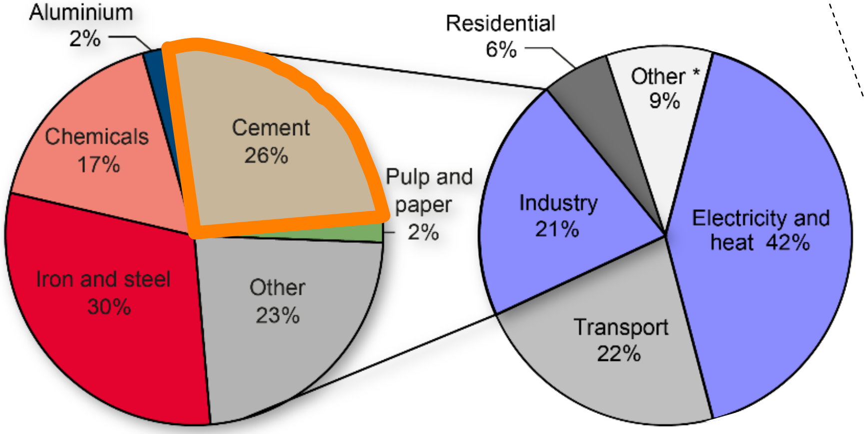
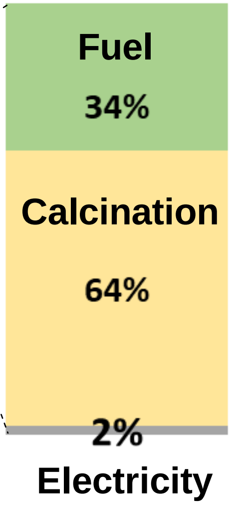
# Talk outline

- **Introduction**
- **Scope** of the study
- **Pilot plant tests** of the $CO_2$ absorber
- **Rate-based model development**
- Rate-based model **assessment** using pilot plant test results
- **Conclusions**

# $CO_2$ emissions from cement

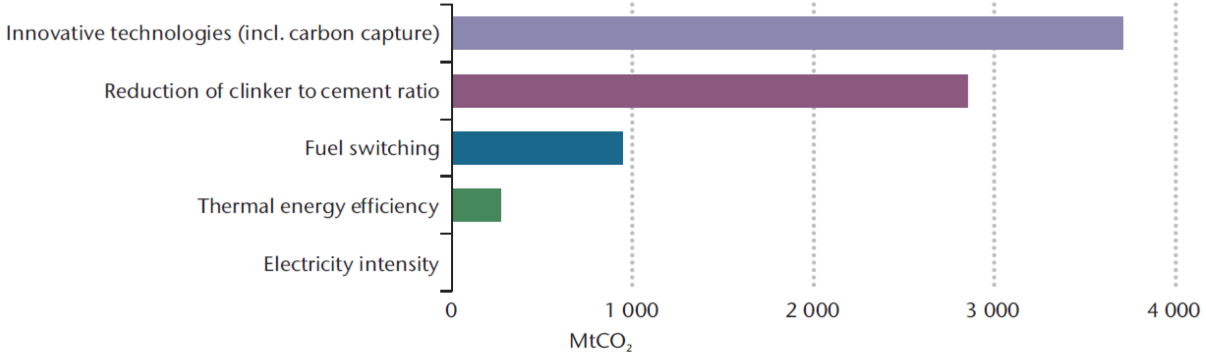
**2.2 Gt $CO_2$ <> 7% global $CO_2$ emissions**





- $CO_2$ emissions intrinsic to the cement manufacturing process
- Higher $CO_2$ concentration in the flue gas with respect to only combustion

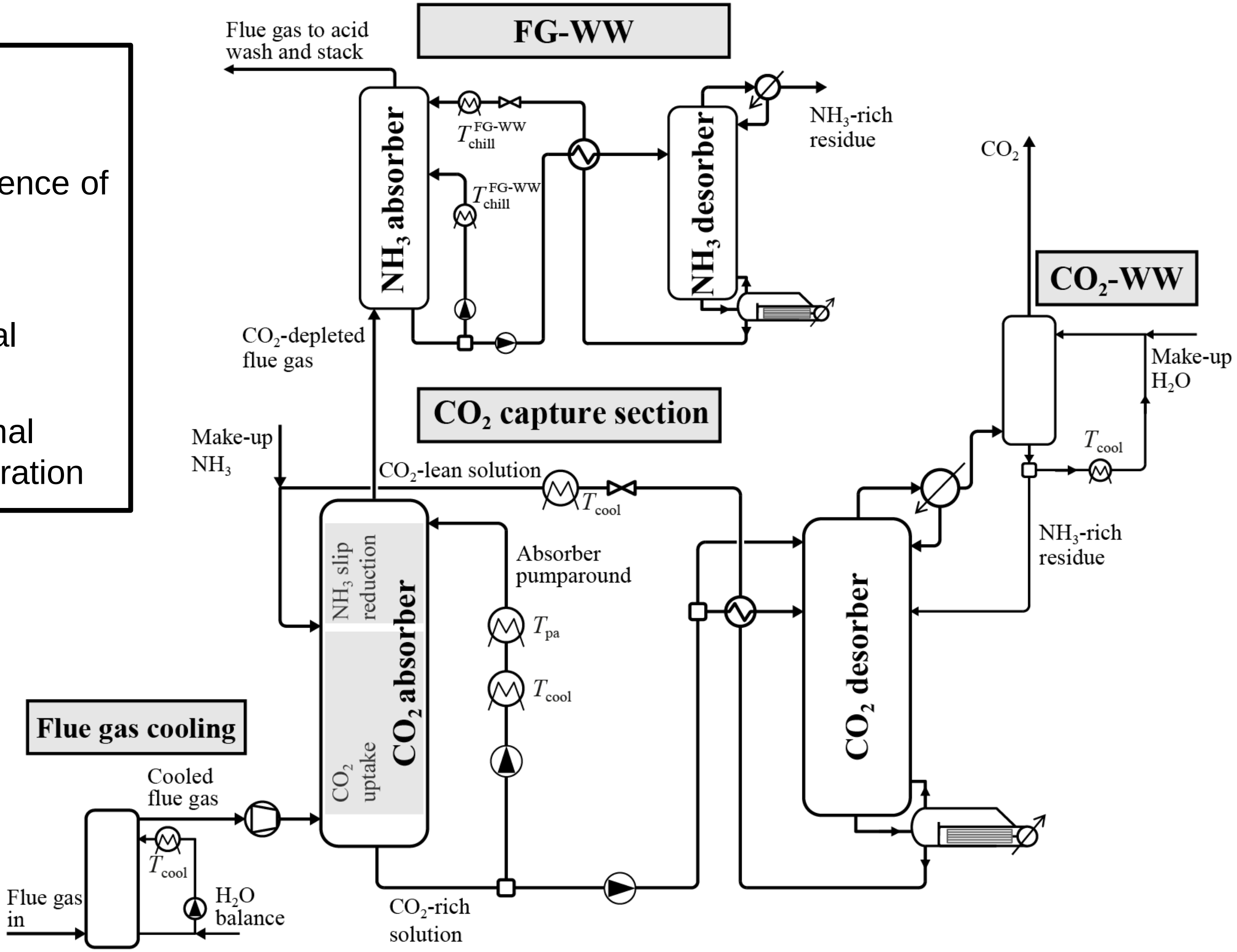
**Global cumulative $CO_2$ emissions reductions 2020-2050**



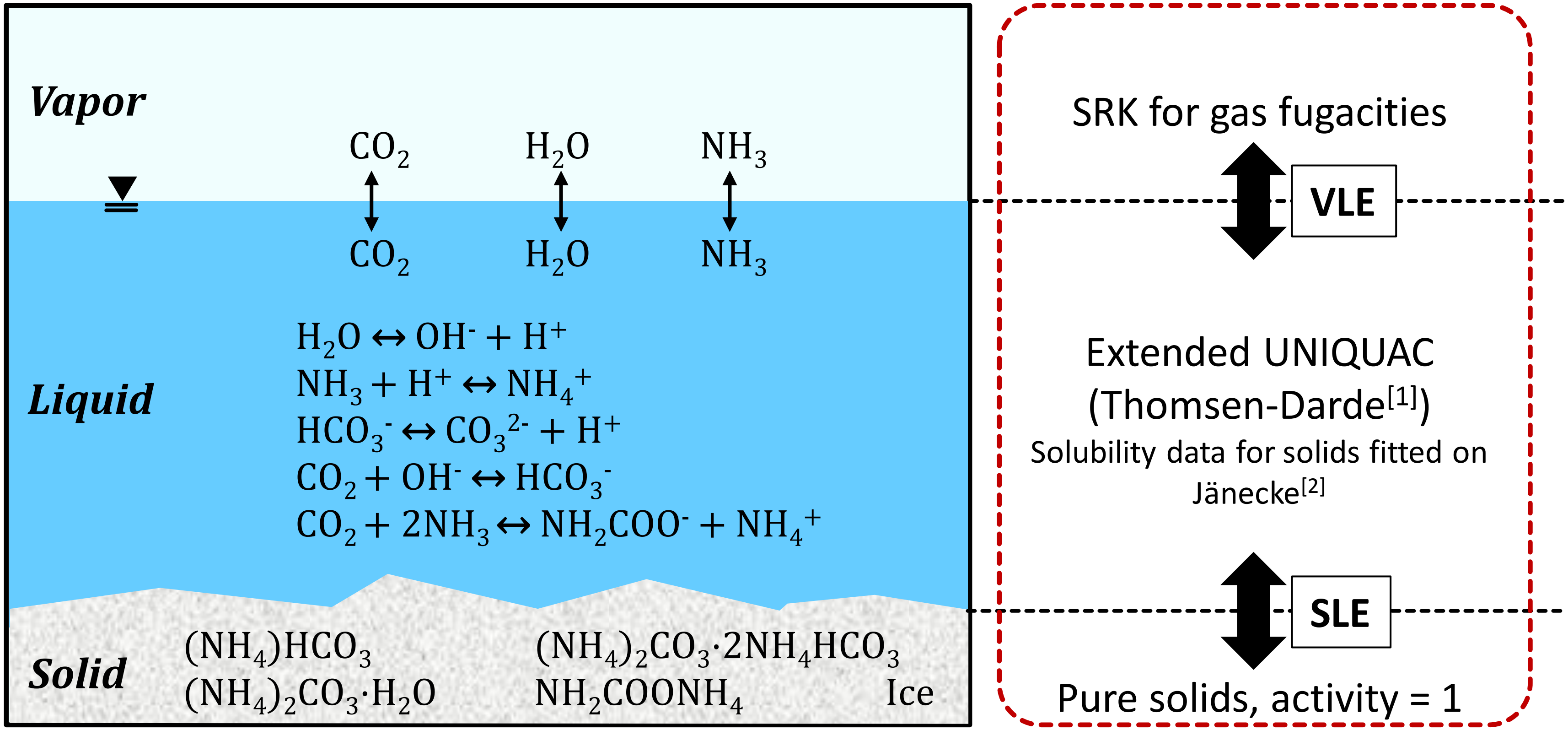
Source: International Energy Agency and Cement Sustainability Initiative (2018) Technology Roadmap – Low-Carbon Transition in the Cement Industry.

# The Chilled Ammonia Process

- Similar process complexity
- Stable in the presence of impurities
- Global availability
- Low environmental footprint and cost
- Competitive thermal energy for regeneration



# The $CO_2$-$NH_3$-$H_2O$ system



**Vapor**

$CO_2$ $H_2O$ $NH_3$

$\updownarrow$ $\updownarrow$ $\updownarrow$

$CO_2$ $H_2O$ $NH_3$

**Liquid**

$H_2O \leftrightarrow OH^- + H^+$

$NH_3 + H^+ \leftrightarrow NH_4^+$

$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$

$CO_2 + OH^- \leftrightarrow HCO_3^-$

$CO_2 + 2NH_3 \leftrightarrow NH_2COO^- + NH_4^+$

**Solid**

$(NH_4)HCO_3$

$(NH_4)_2CO_3 \cdot H_2O$

$(NH_4)_2CO_3 \cdot 2NH_4HCO_3$

$NH_2COONH_4$

Ice

SRK for gas fugacities

**VLE**

Extended UNIQUAC (Thomsen-Darde[1])

Solubility data for solids fitted on Jänecke[2]

**SLE**

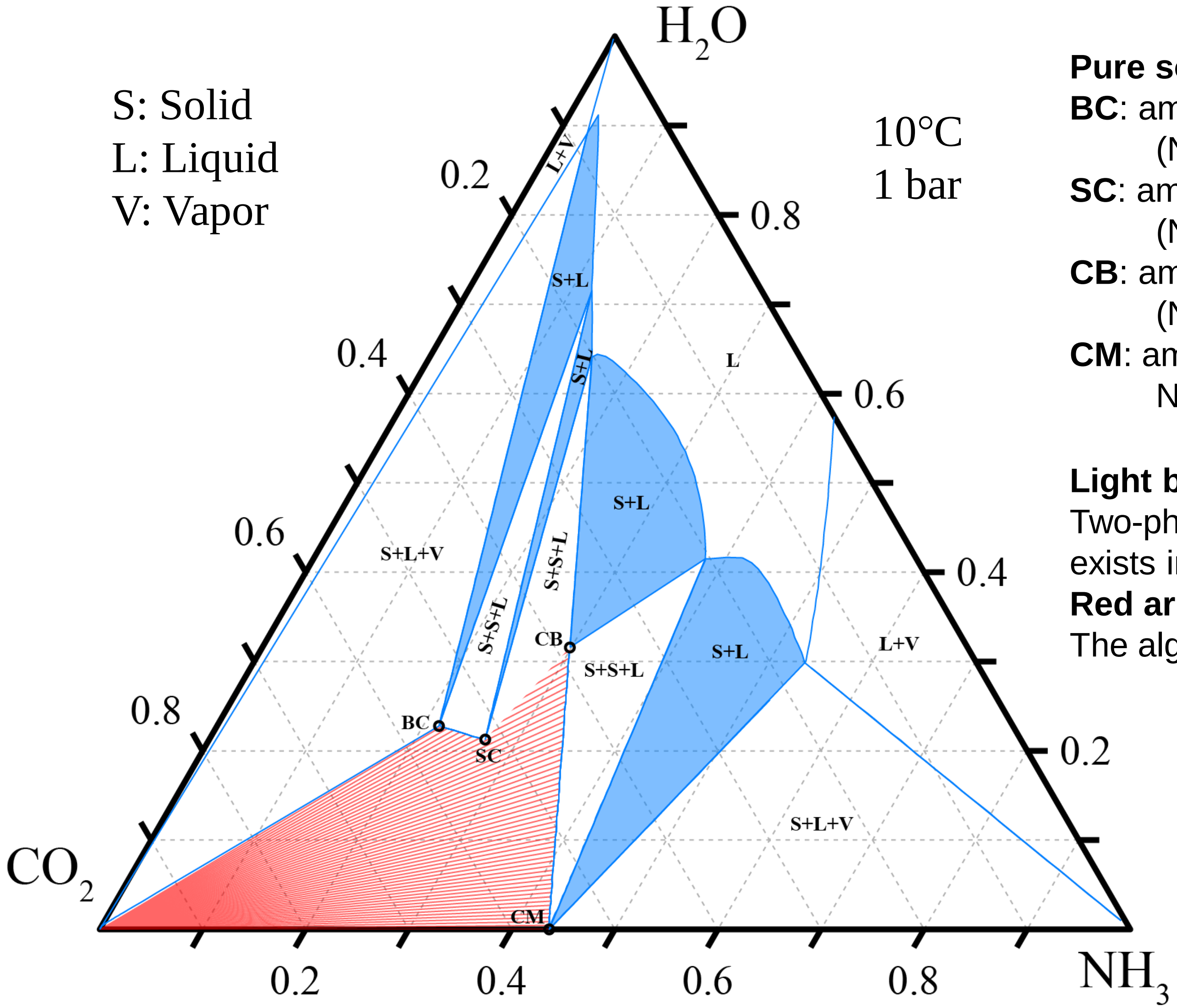
Pure solids, activity = 1

**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

# Phase diagram: $CO_2$-$NH_3$-$H_2O$ system



**Pure solids**

**BC**: ammonium bicarbonate $(NH_4)HCO_3$

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

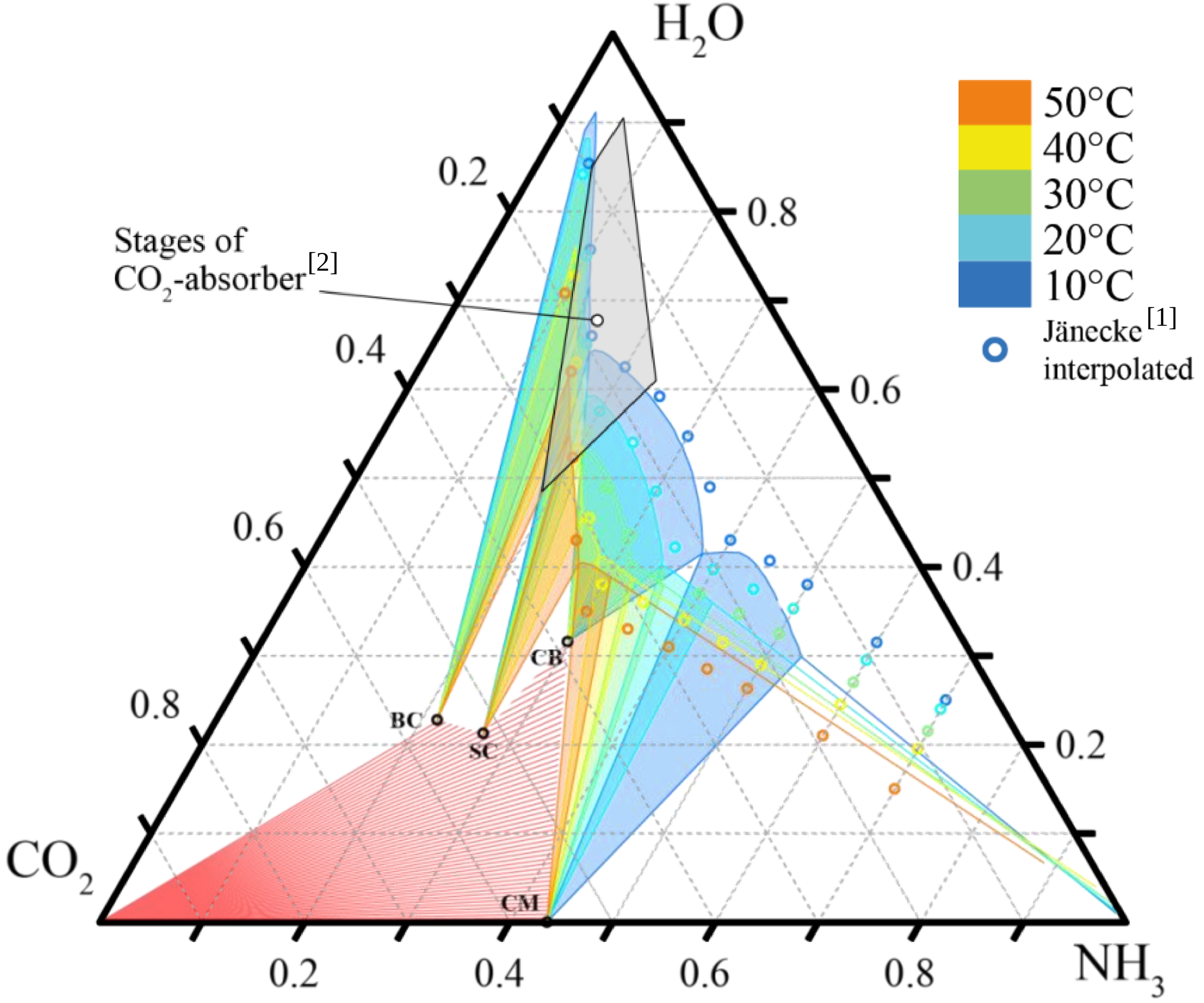
**CB**: ammonium carbonate $(NH_4)_2CO_3 \cdot H_2O$

**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

# Phase diagram: $CO_2$-$NH_3$-$H_2O$ system



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

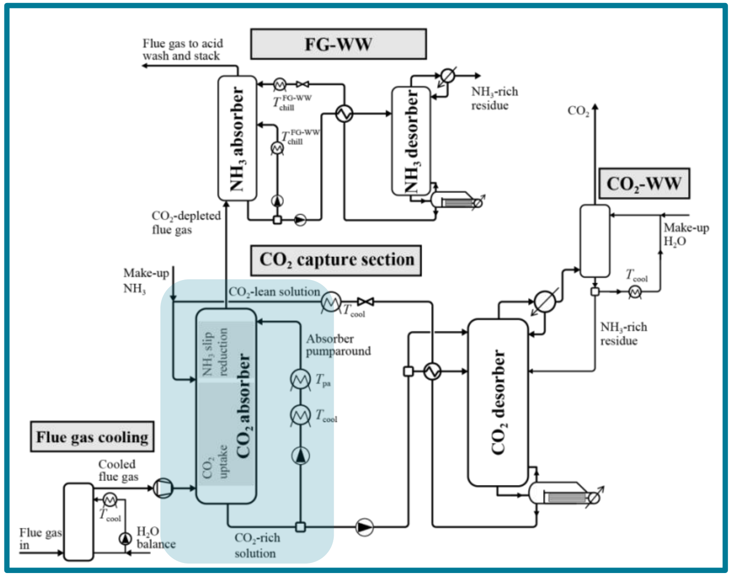
[2] Sutter et al. *Chem Eng Sci* 133 (2015) 170-180

# 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. $CO_2$



**Change of operating conditions in the $CO_2$ absorber**

## Research question:

**Are the available rate-based models valid or do they require adaptations?**

**1**

**Pilot plant $CO_2$ absorption tests**

**2**

**Validation of rate-based models** from literature

**3**

**Development of new rate-based model**

**4**

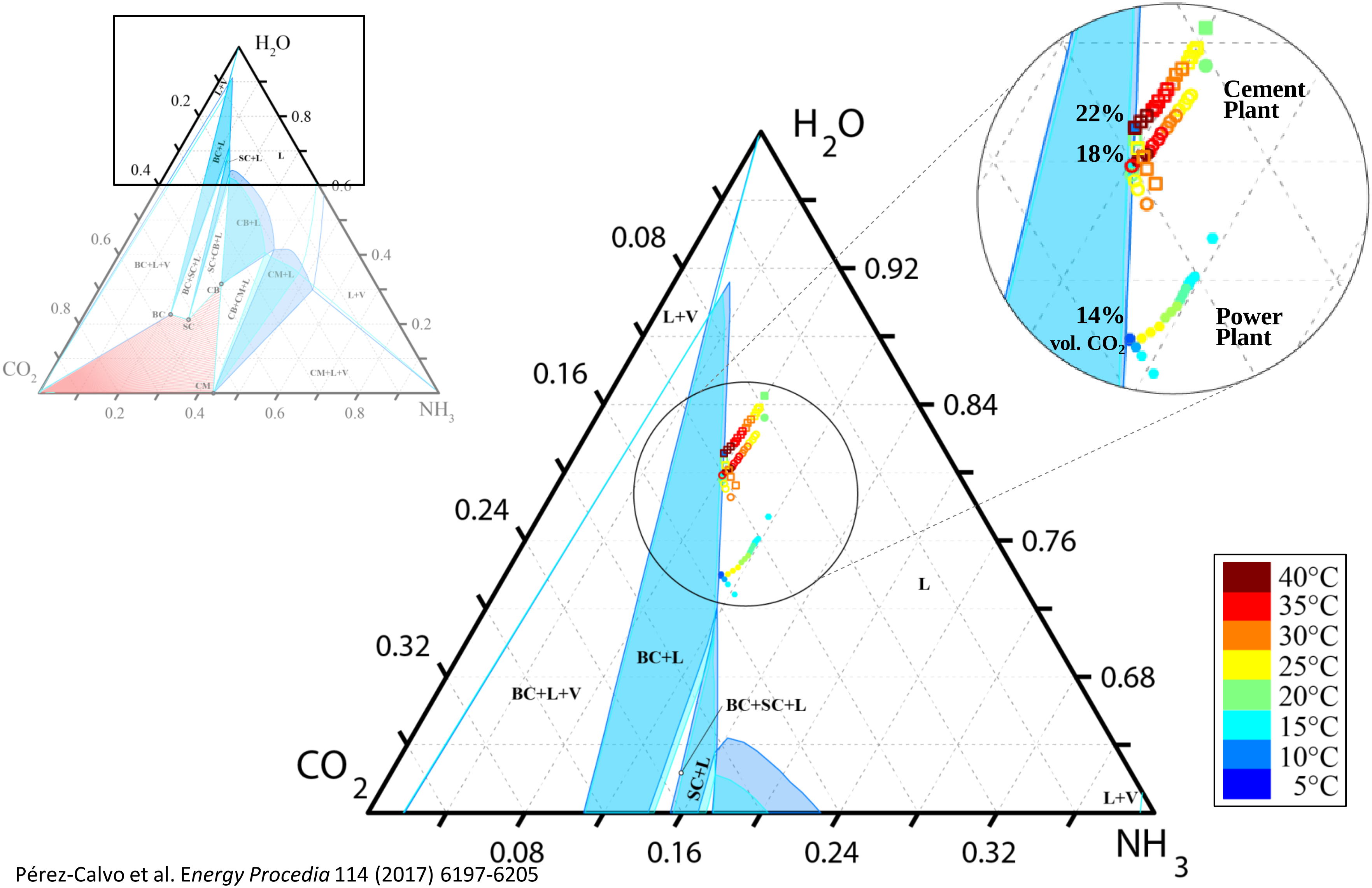
**Assessment of new rate-based model performance**

# Test matrix definition

| | $CO_2$ content in flue gas (%vol) | Packing type | Liquid properties |
|---|---|---|---|
| CSIRO[1] | 8.5 – 12 | Random<br>25 mm Pall ring | |
| **This work** | Up to 35 | Structured<br>Flexipac M 350X | |

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

# Test matrix definition: Preliminary process optimization



Pérez-Calvo et al. *Energy Procedia* 114 (2017) 6197-6205

# Test matrix definition: Preliminary process optimization

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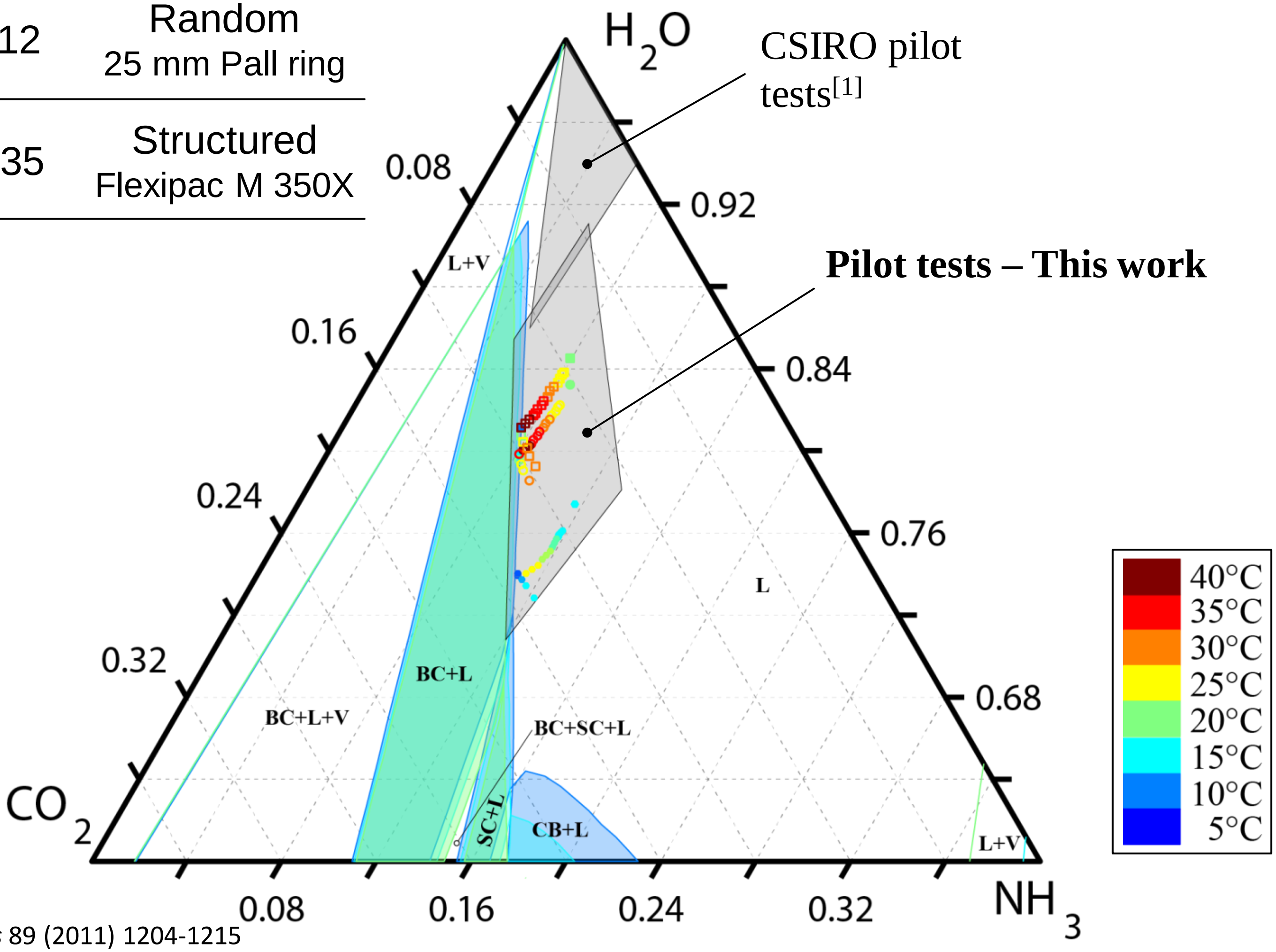
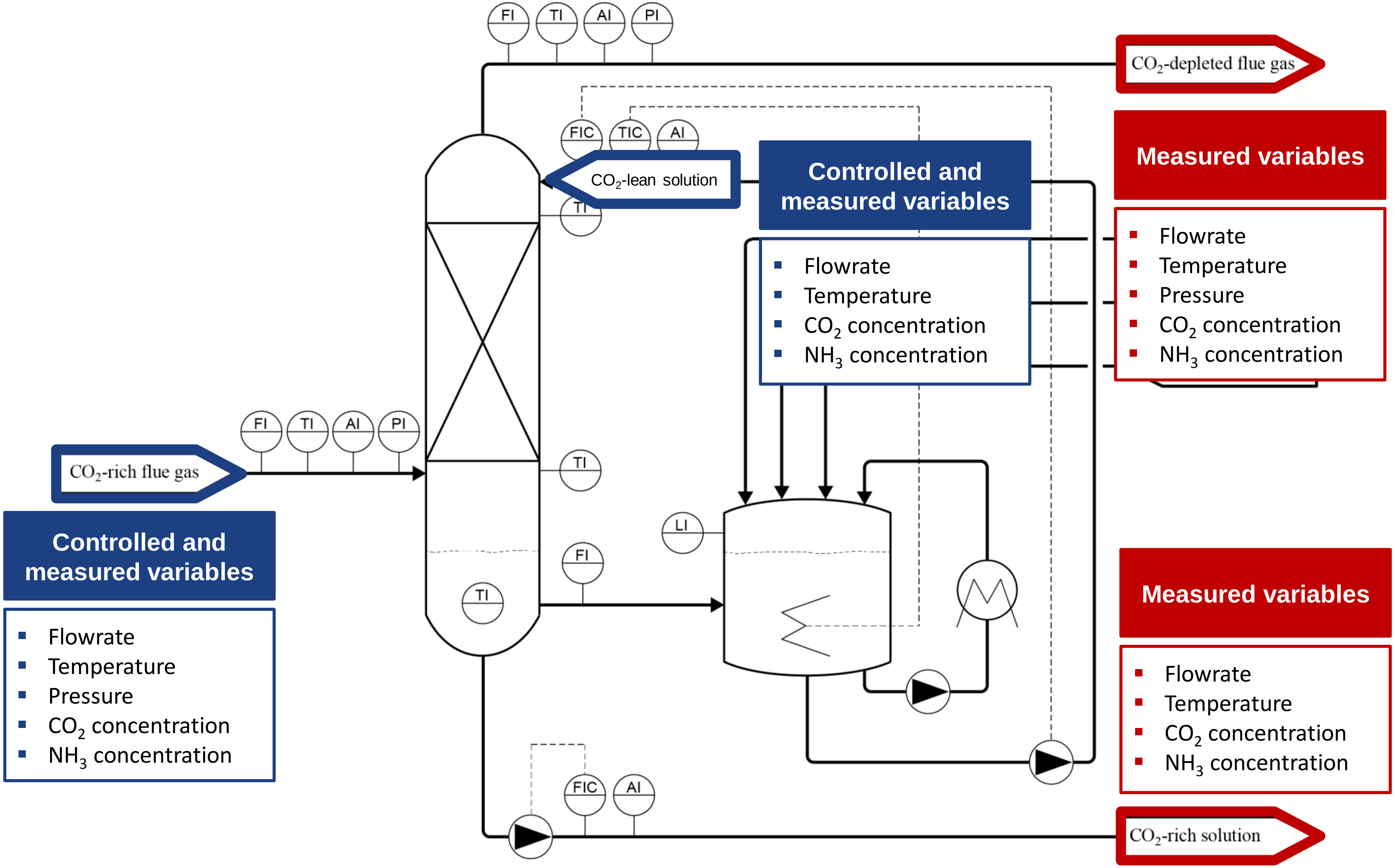


CSIRO pilot tests[1]

**Pilot tests – This work**

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

# Test rig



**Controlled and measured variables**

- Flowrate
- Temperature
- $CO_2$ concentration
- $NH_3$ concentration

**Measured variables**

- Flowrate
- Temperature
- Pressure
- $CO_2$ concentration
- $NH_3$ concentration

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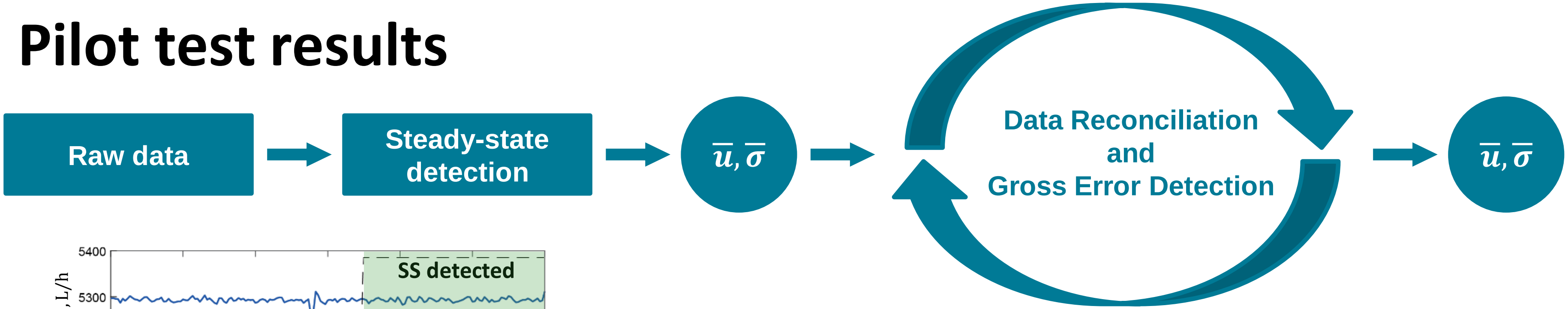
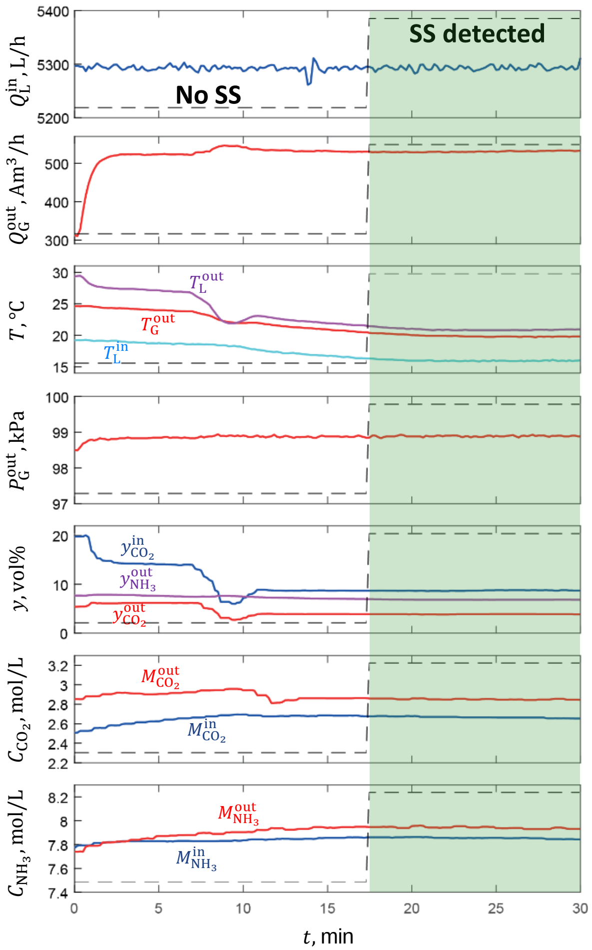
**Measured variables**

- Flowrate
- Temperature
- $CO_2$ concentration
- $NH_3$ concentration

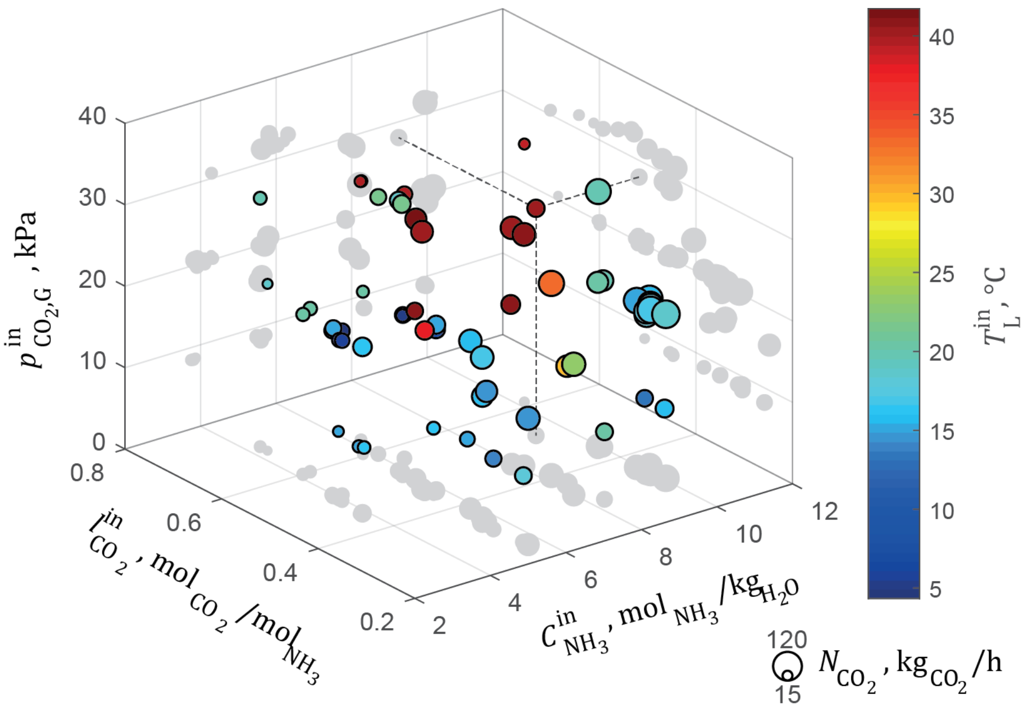
# Pilot test results



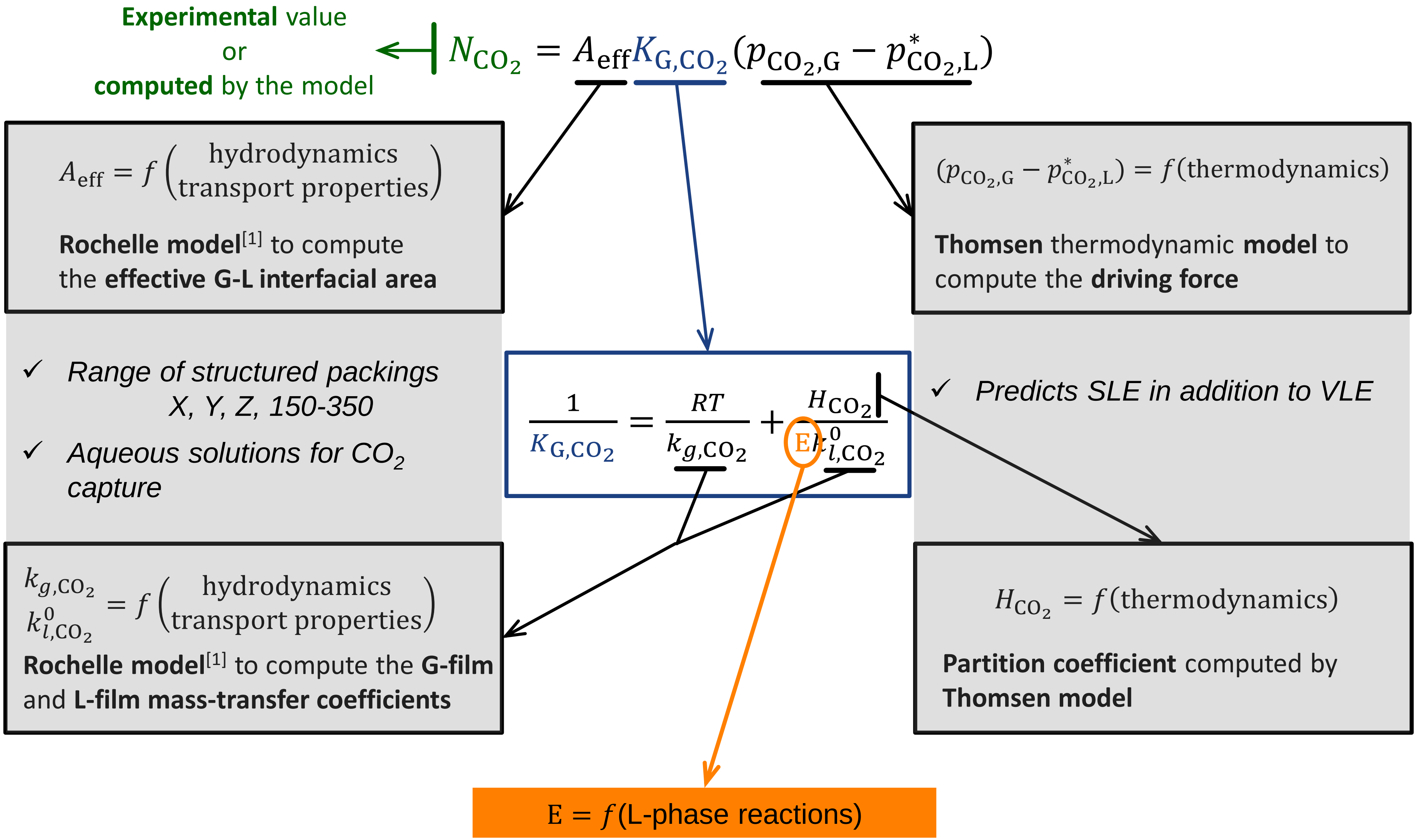
**Raw data** → **Steady-state detection** → $\bar{u}, \bar{\sigma}$ → **Data Reconciliation and Gross Error Detection** → $\bar{u}, \bar{\sigma}$



## 82 experimental points



# Rate-based model



**Experimental** value
or
**computed** by the model

$$N_{CO_2} = \underline{A_{eff}}\,\underline{K_{G,CO_2}}\,\underline{(p_{CO_2,G} - p^*_{CO_2,L})}$$

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

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

- ✓ *Range of structured packings X, Y, Z, 150-350*
- ✓ *Aqueous solutions for $CO_2$ capture*

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

$$(p_{CO_2,G} - p^*_{CO_2,L}) = f(\text{thermodynamics})$$

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

- ✓ *Predicts SLE in addition to VLE*

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

**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**

$\mathrm{E} = f$(L-phase reactions)

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

# L-phase reaction kinetics – Validation of literature models

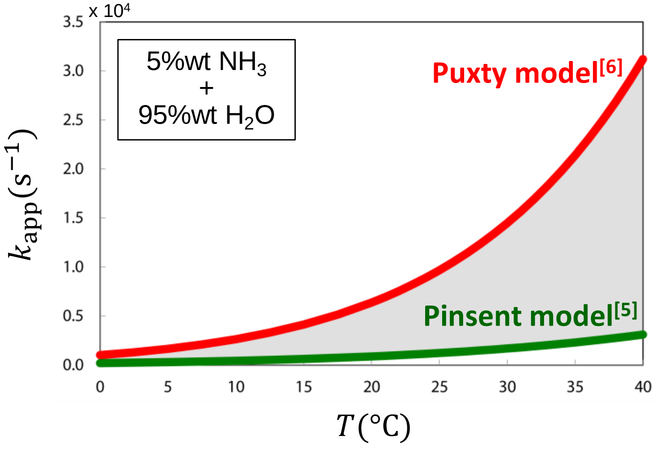
$$CO_2 + \cancel{OH^-} \xrightarrow{k_{bc}} HCO_3^-$$

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

➔ **Single irreversible reaction**[1,2] ➔ $E = f(\mathrm{Ha})$[3,4]

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

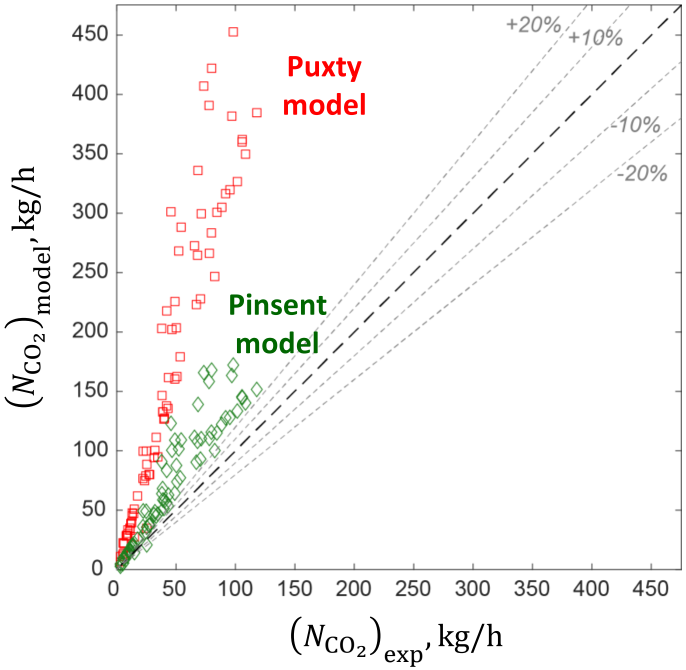
$$r_{cm} = k_{app} C_{CO_2}$$



**Simple mechanism**

$$\begin{cases} CO_2 + NH_3 \rightarrow NH_2COO^- + H^+ \\ NH_3 + H^+ \rightarrow NH_4^+ \end{cases}$$

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



[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
[4] Levenspiel (3rd ed.) (1999) *Chemical Reaction Engineering*. New York: John Wiley & Sons
[5] Pinsent et al. *Trans Faraday Soc.* 52 (1956) 1594-1598
[6] Puxty et al. *Chem Eng Sci.* 65 (2009) 915-922

# L-phase reaction kinetics – Parameter estimation

$$\left.\begin{array}{l} CO_2 + \cancel{OH^-} \xrightarrow{k_{bc}} HCO_3^- \\ CO_2 + 2NH_3 \xrightarrow{k_{cm}} NH_2COO^- + NH_4^+ \end{array}\right\}$$

➔ **Single irreversible reaction** ➔ $E = f(\mathrm{Ha})$

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

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

**Termolecular mechanism**

$$\begin{cases} CO_2 + 2NH_3 \rightarrow NH_2COO^- + NH_4^+ \\ CO_2 + NH_3 + H_2O \rightarrow NH_2COO^- + H_3O^+ \end{cases}$$

**Zwitterion mechanism**

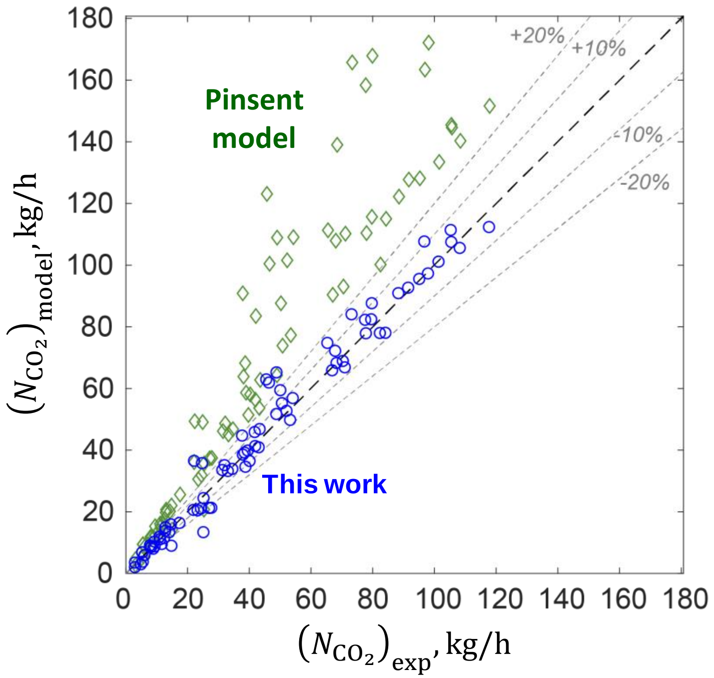
$$\begin{cases} CO_2 + NH_3 \leftrightarrow NH_3^+COO^- \\ NH_3^+COO^- + NH_3 \rightarrow NH_2COO^- + NH_4^+ \\ NH_3^+COO^- + H_2O \rightarrow NH_2COO^- + H_3O^+ \end{cases}$$

**Empirical expression**

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

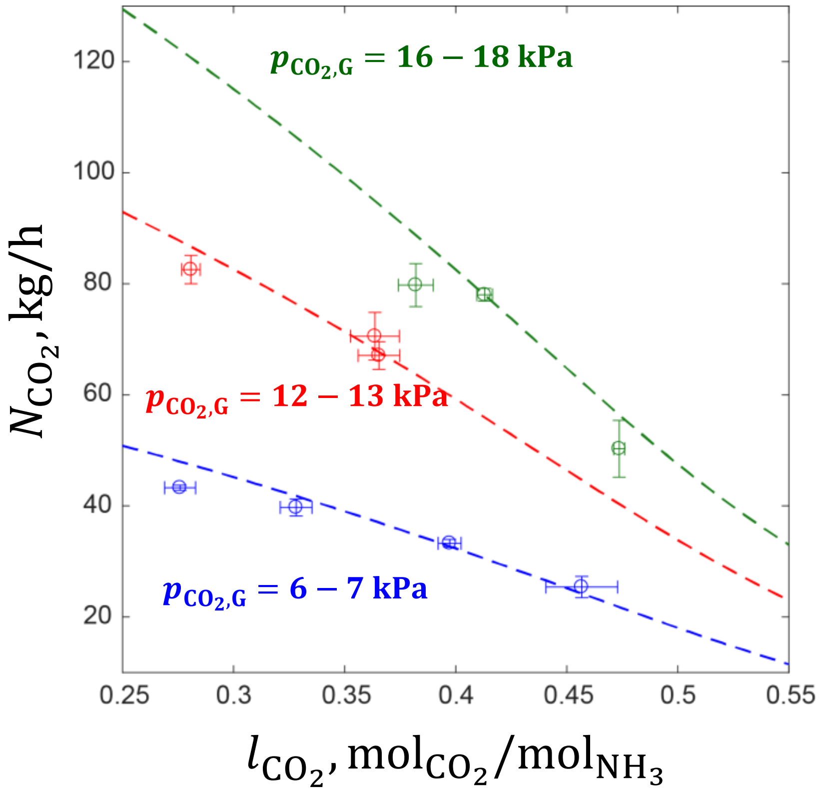
$$1 \leq n \leq 2$$

| | $k_{cm}(T = T_{ref} = 298\ \mathrm{K})$ $\left[\frac{m^3}{kmol\ s}\right]$ | $E_{a,cm}$ $\left[\frac{kJ}{kmol}\right]$ | $n$ $[-]$ |
|---|---|---|---|
| This work | 167 | 27,800 | 1.3 |
| Pinsent | 431 | 48,500 | 1 |



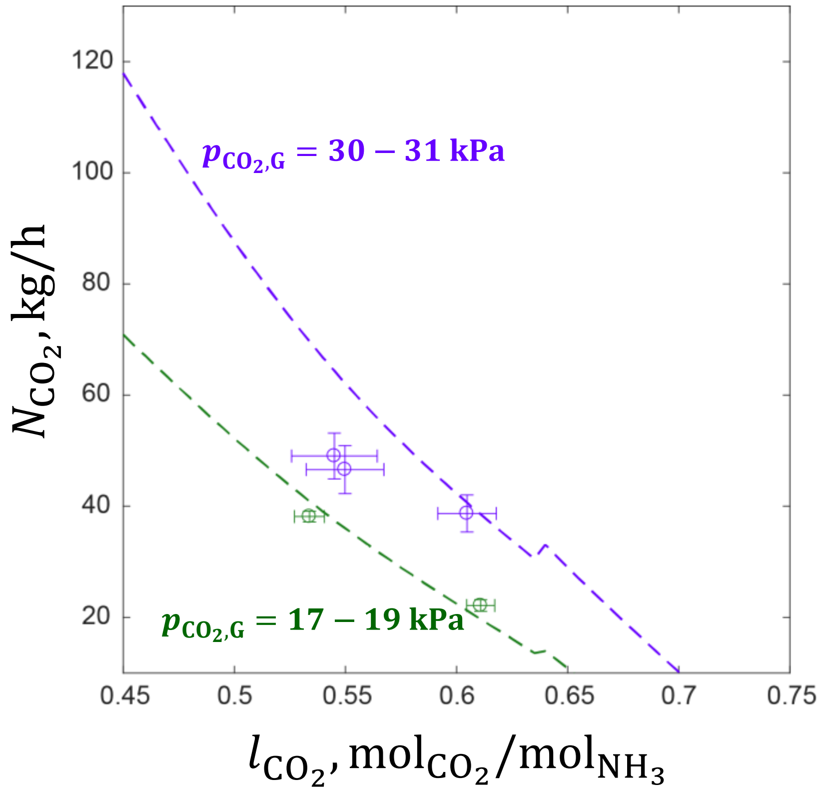
# Rate-based model performance assessment (1)

## Set A – low $CO_2$ loading



$C_{NH_3} = 5.5 - 5.8$ m
$T_L = 16 - 20$°C
$\frac{L}{G} = 8.5 - 8.8$ kg/kg
$v_{s,G} = 0.9 - 1.0$ m/s

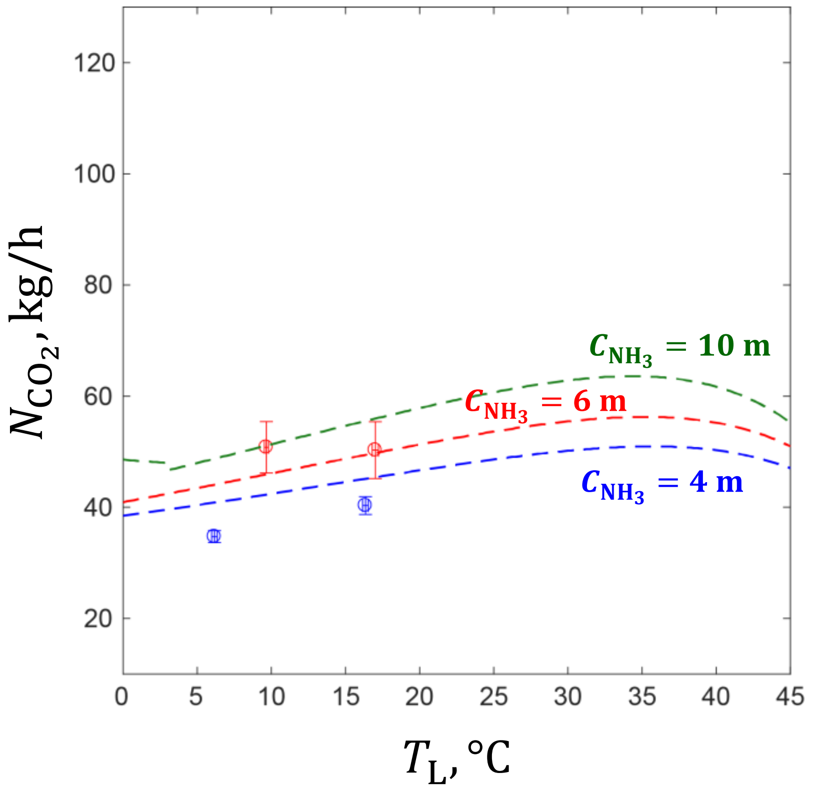
## Set B – high $CO_2$ loading



$C_{NH_3} = 5.8 - 6.1$ m
$T_L = 20 - 23$°C
$\frac{L}{G} = 10.7 - 11.5$ kg/kg
$v_{s,G} = 0.7$ m/s

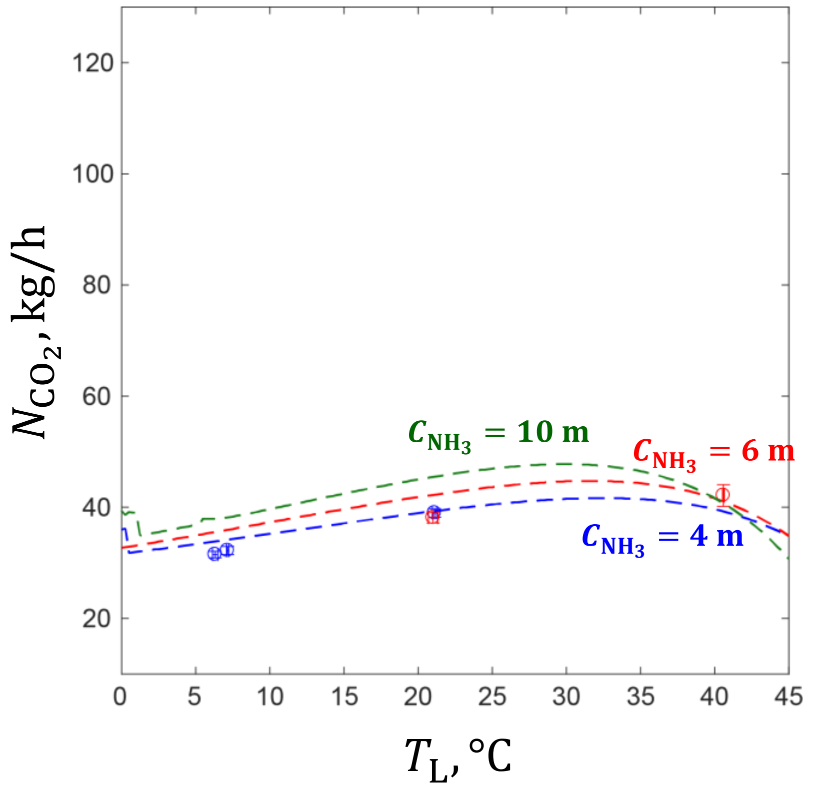
# Rate-based model performance assessment (2)

## Set C – low $CO_2$ loading



$p_{CO_2,G} = 18 - 19$ kPa
$l_{CO_2} = 0.47 - 0.54\ \text{mol}_{CO_2}/\text{mol}_{NH_3}$
$\frac{L}{G} = 7.6 - 8.8$ kg/kg
$v_{s,G} = 0.9 - 1.1$ m/s

## Set D – high $CO_2$ loading



$p_{CO_2,G} = 17 - 19$ kPa
$l_{CO_2} = 0.52 - 0.54\ \text{mol}_{CO_2}/\text{mol}_{NH_3}$
$\frac{L}{G} = 10.7 - 11.4$ kg/kg
$v_{s,G} = 0.7$ m/s

# Conclusions

- The **Chilled Ammonia Process** is a **very promising** technology for **$CO_2$ capture from cement plants**
  - It has been **confirmed experimentally** that the **higher $CO_2$ concentration** in the flue gas **enhances the absorption of $CO_2$**
  - **$CO_2$ capture efficiencies as high as 60%** have been obtained **in only 3 m high** packing
- The results of the **$CO_2$ absorption pilot plant tests** have **shown** that the **rate-based models available in the literature** are **outside their range of validity when** used at the conditions of the CAP **applied to cement plants**
- Therefore, **a new rate-based model has been developed**, that:
  - Is **able to reproduce** the trends of the **$CO_2$ absorption rate obtained experimentally**
  - **Can be used** with engineering purposes **for the simulation and optimization of the CAP applied to cement plants** for $CO_2$ capture

# Acknowledgements

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CEMCAP

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