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

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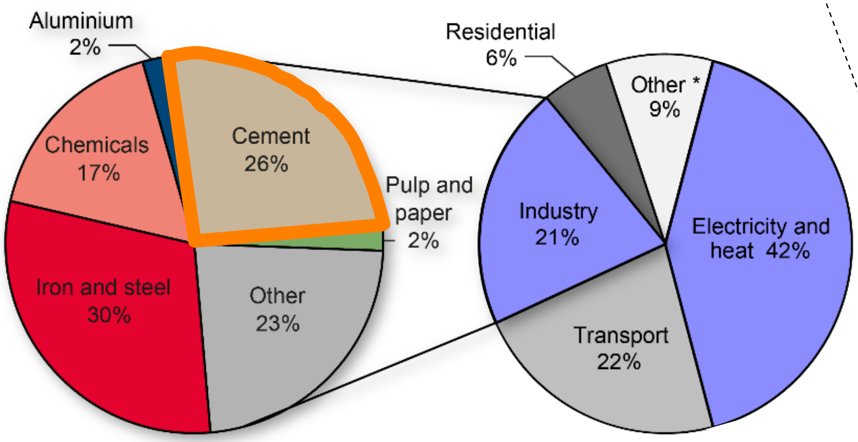
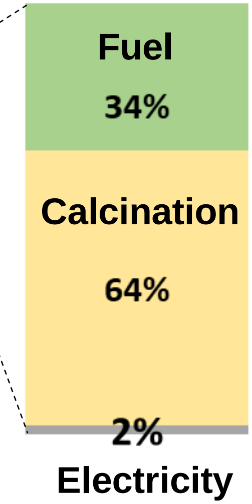
Talk outline

- **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

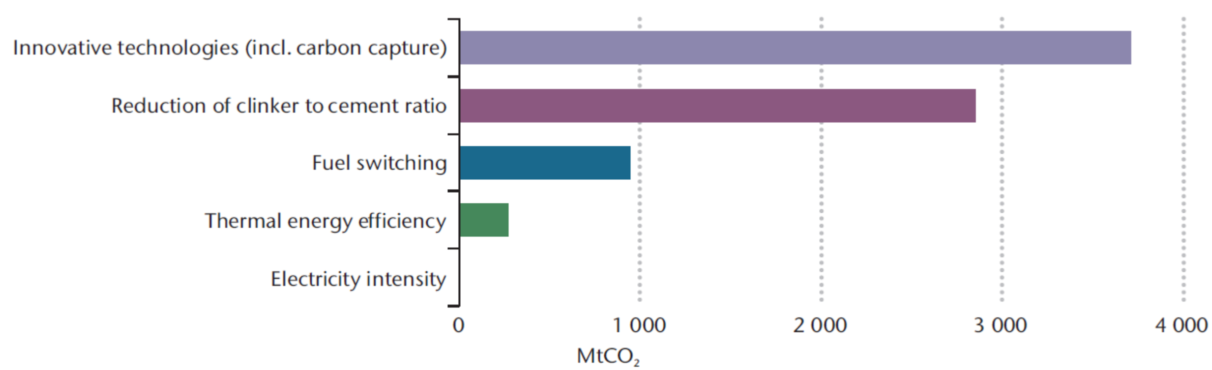
2.2 Gt CO_2 <> 7% global CO_2 emissions





- 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.

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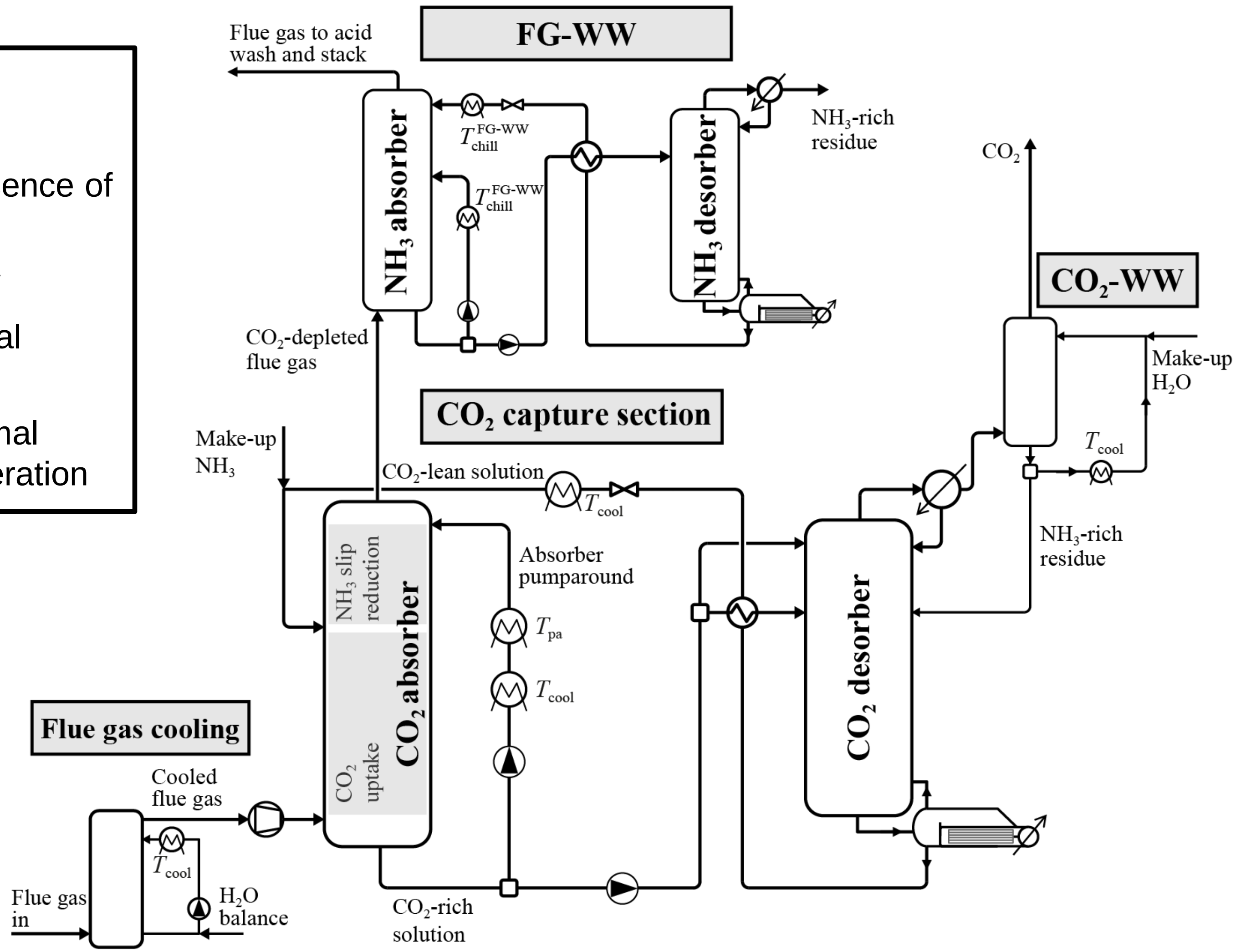
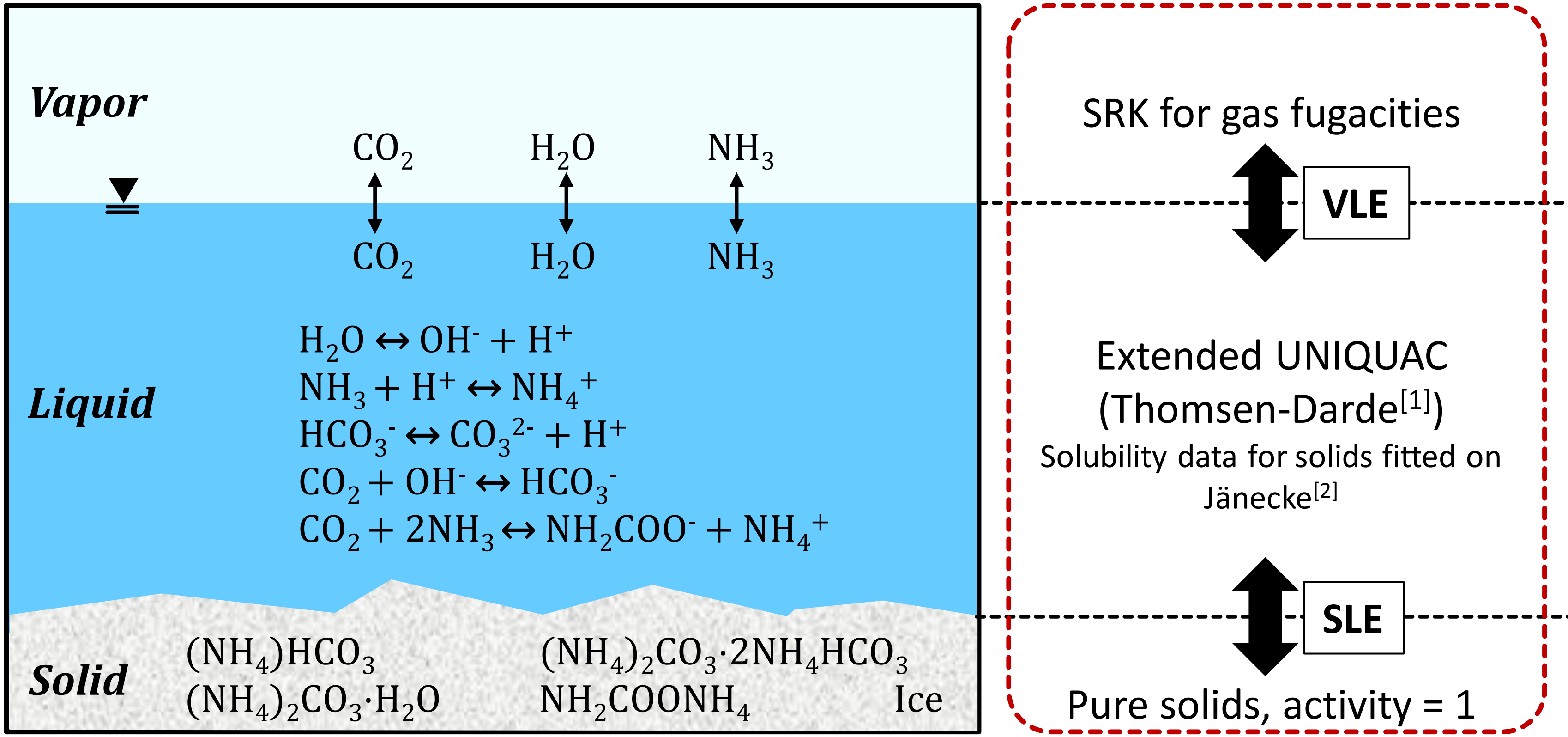
The Chilled Ammonia Process

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



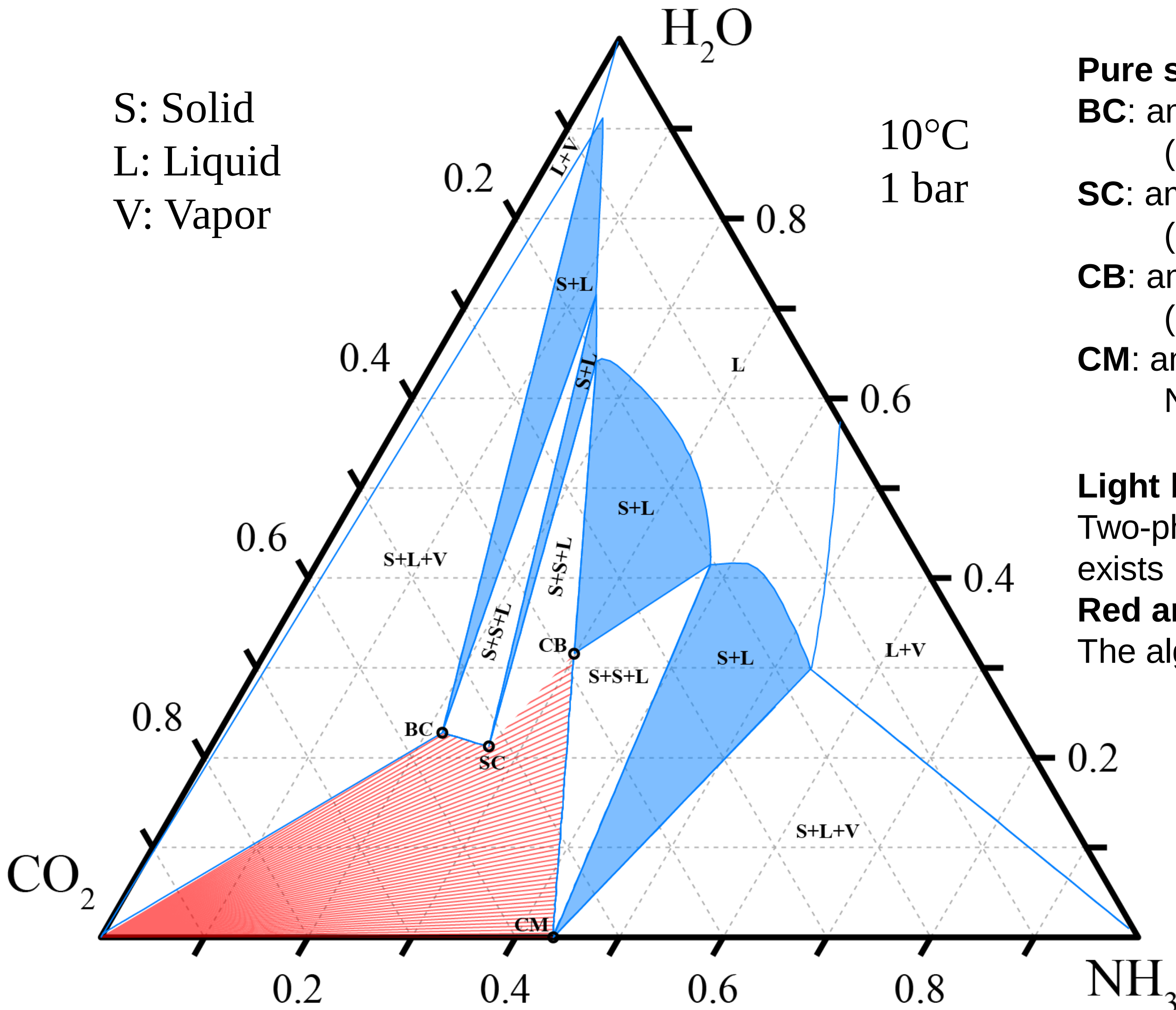
The CO_2-NH_3-H_2O system



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

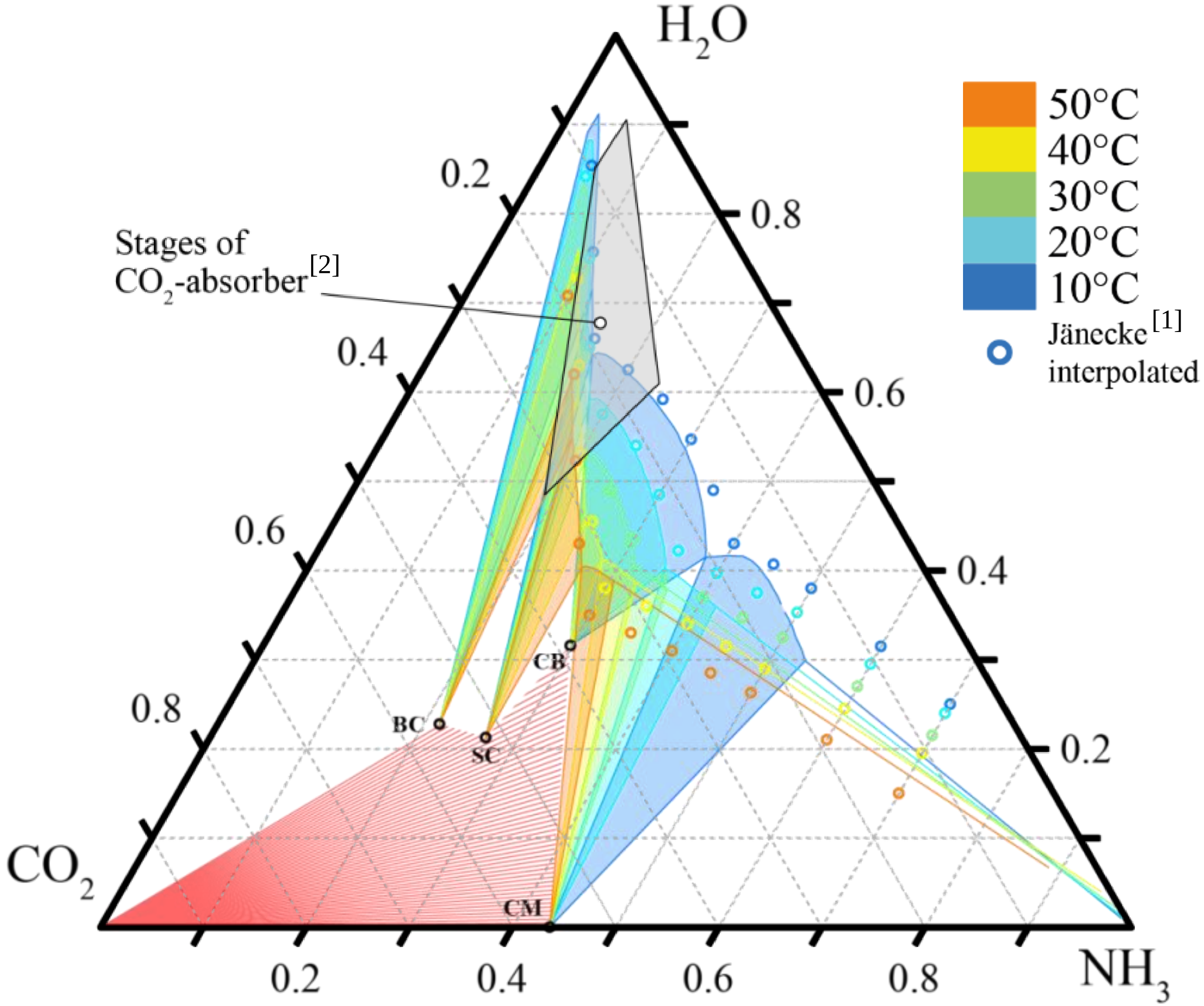
Phase diagram: CO_2-NH_3-H_2O system



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

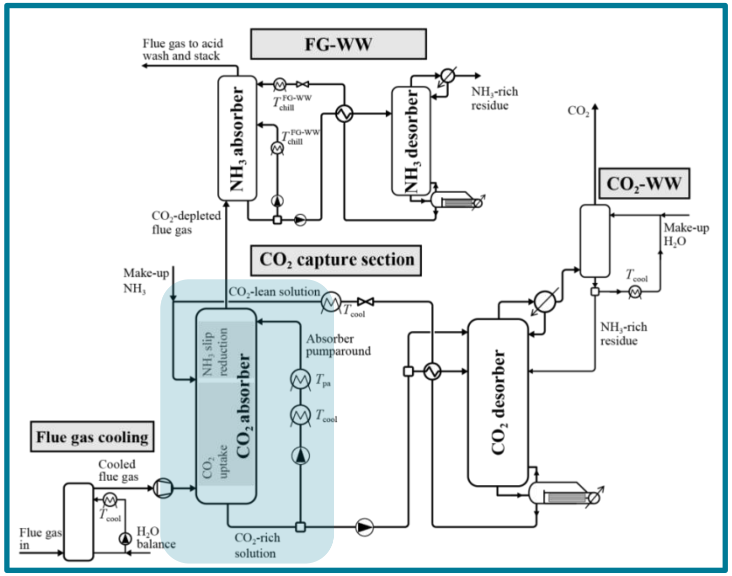
[2] Sutter et al. *Chem Eng Sci* 133 (2015) 170-180

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?

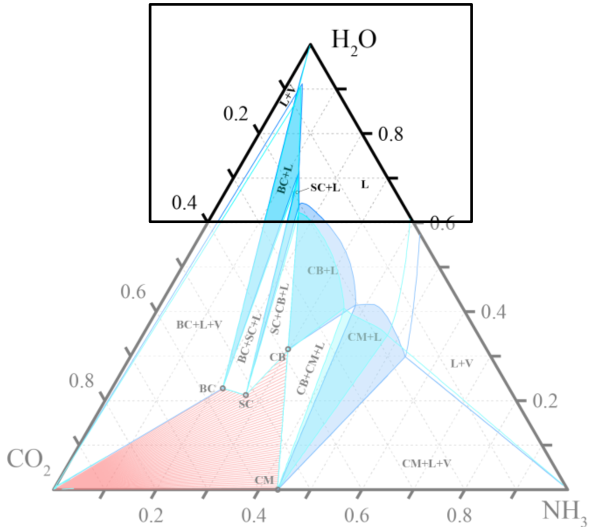
1. **Pilot plant CO_2 absorption tests**
2. **Validation of rate-based models** from literature
3. **Development of new rate-based model**
4. **Assessment of new rate-based model performance**

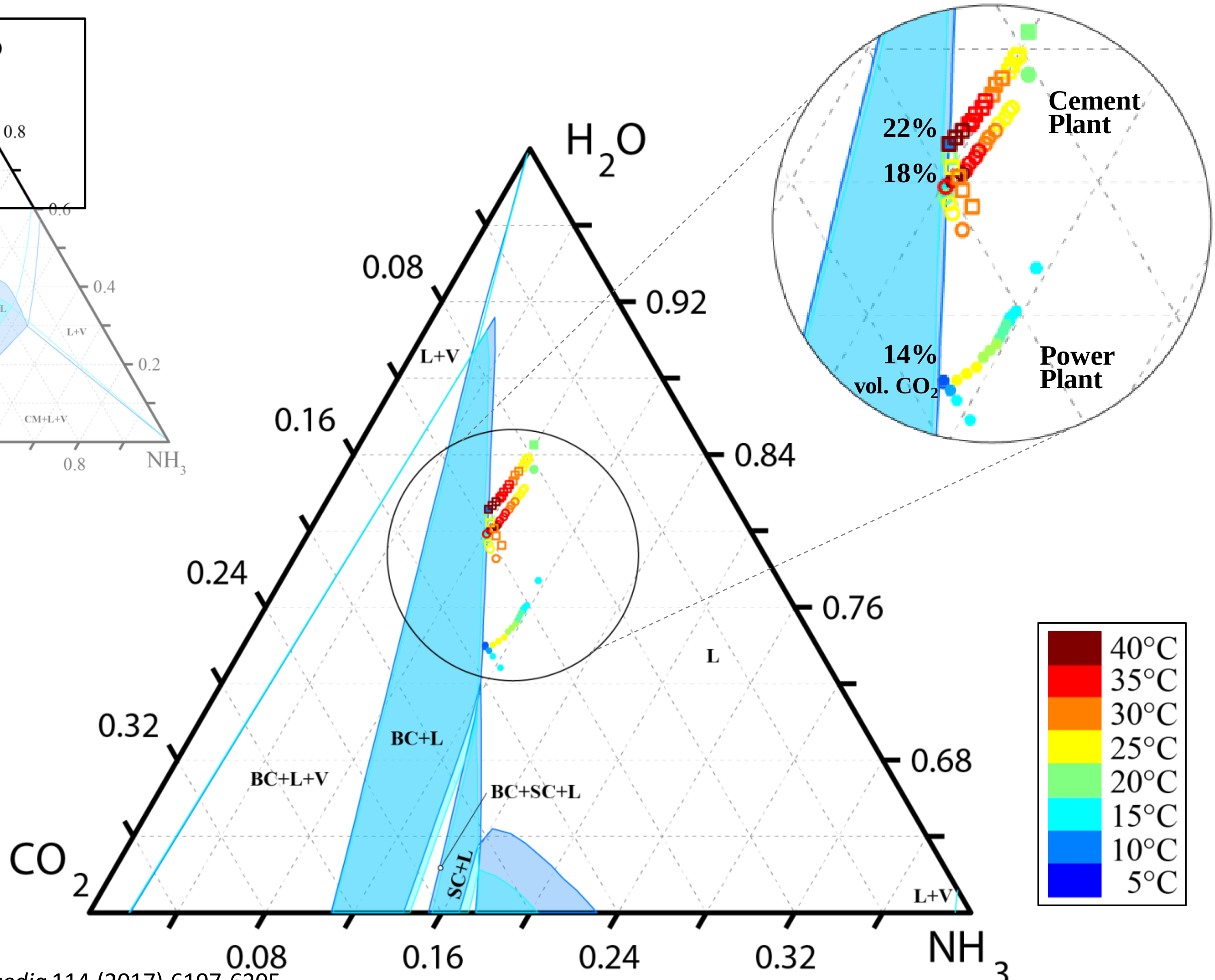
Test matrix definition

	CO_2 content in flue gas (%vol)	Packing type	Liquid properties
CSIRO[1]	8.5 – 12	Random 25 mm Pall ring	
This work	Up to 35	Structured 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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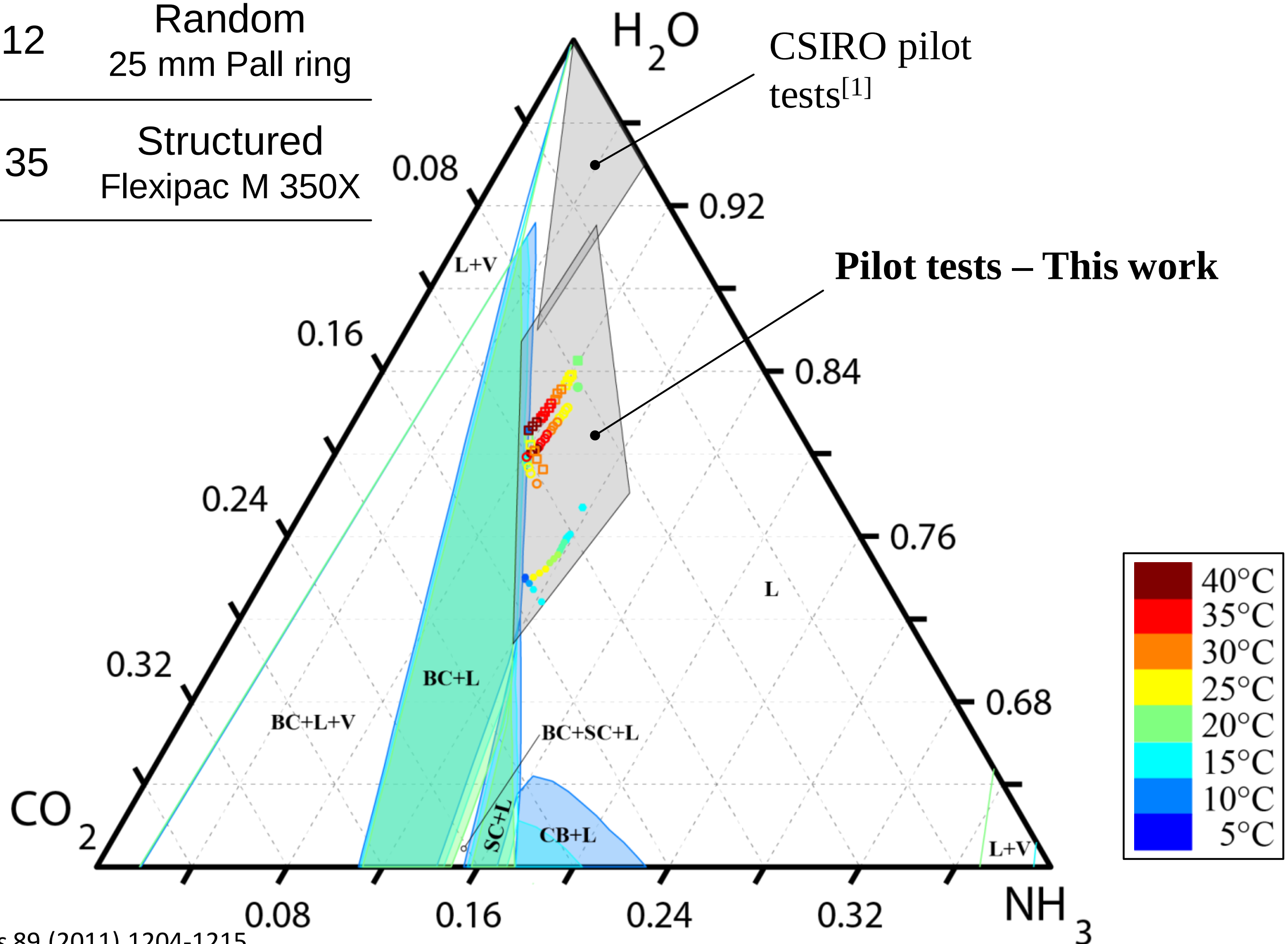
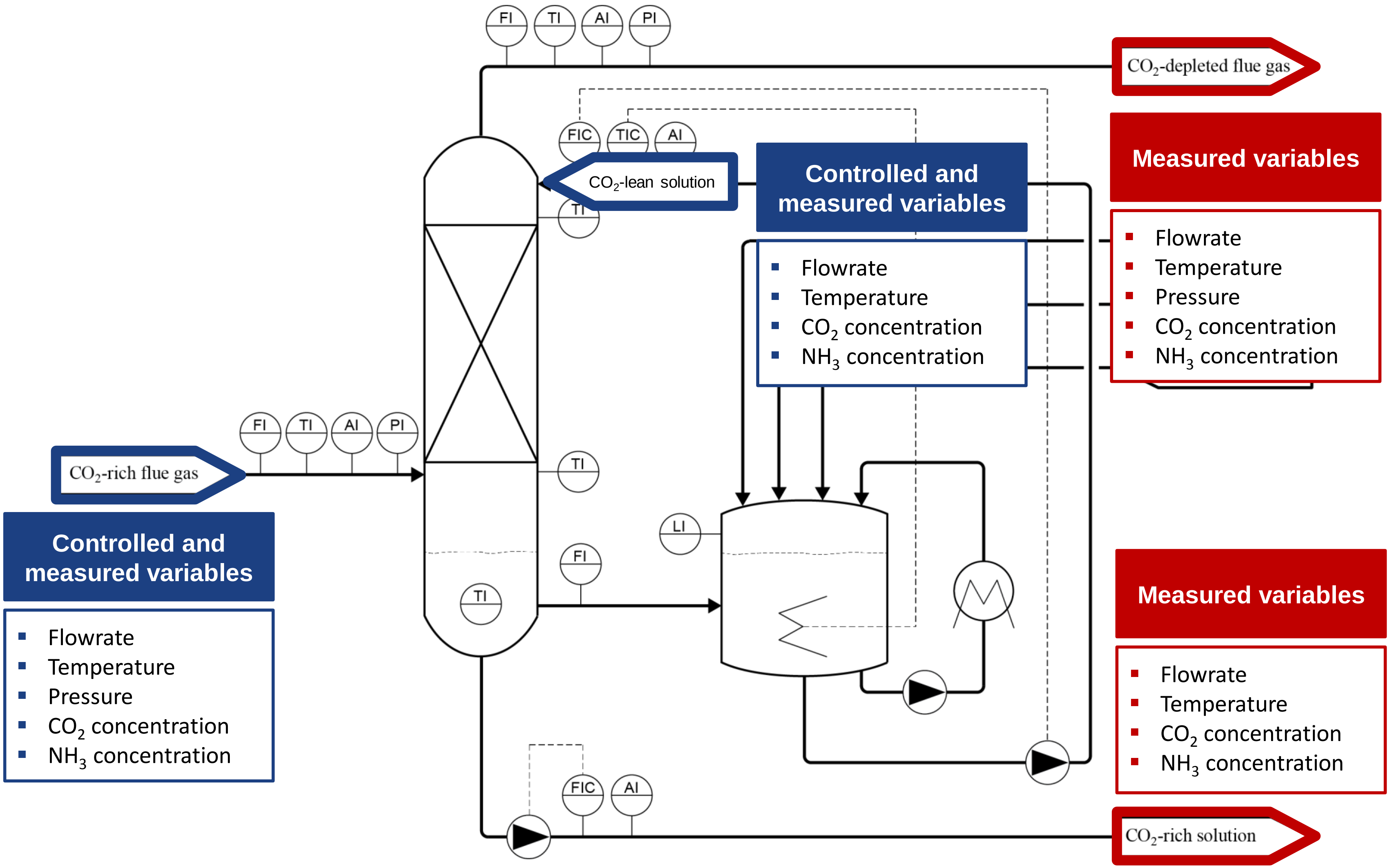
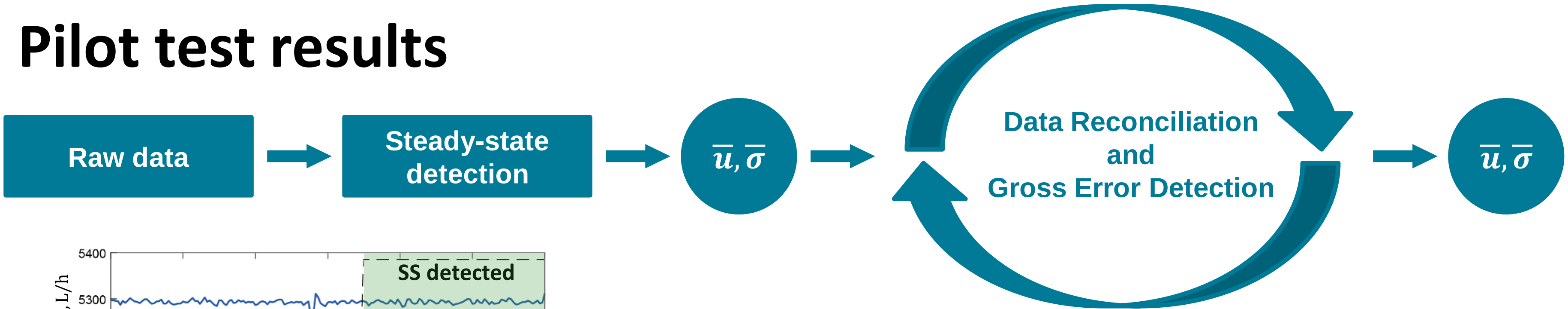


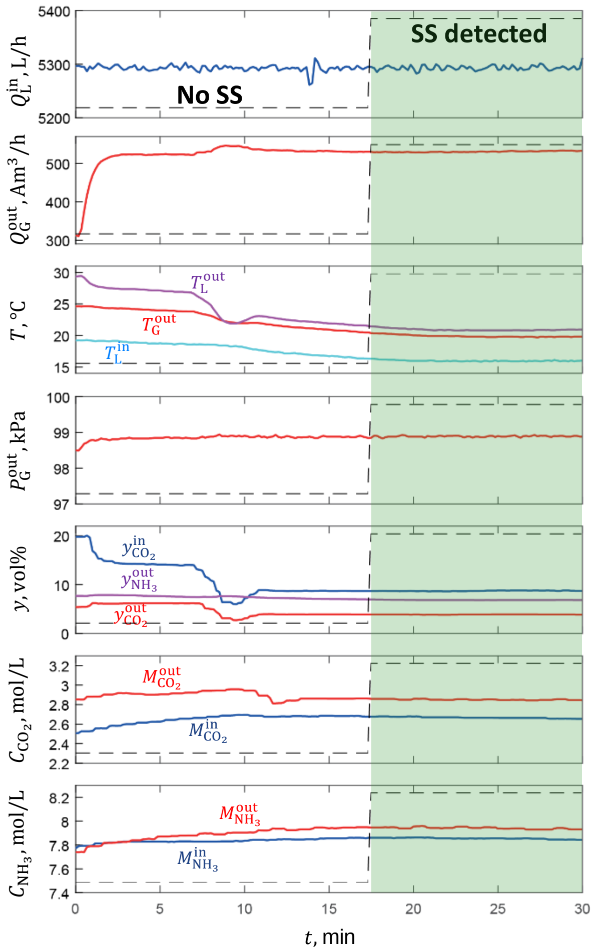
[1] Yu et al. *Chem Eng Res Des* 89 (2011) 1204-1215

Test rig

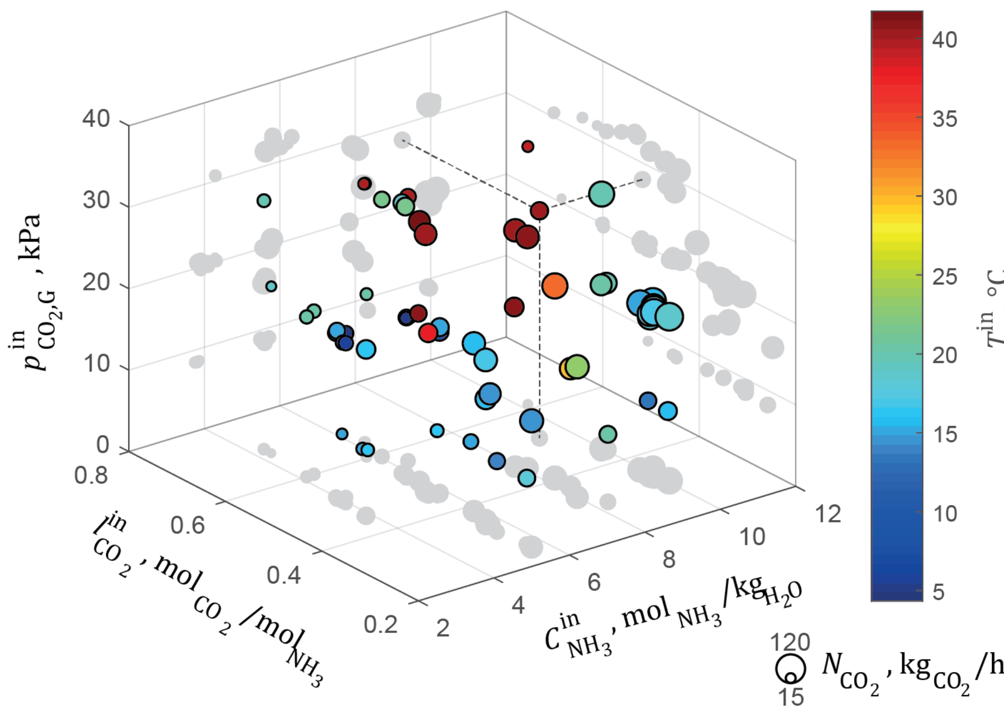

FI
TI
AI
PI
CO_2-depleted flue gas
FIC
TIC
AI
CO_2-lean solution
TI
Controlled and measured variables
- Flowrate
- Temperature
- CO_2 concentration
- NH_3 concentration
Measured variables
- Flowrate
- Temperature
- Pressure
- CO_2 concentration
- NH_3 concentration
FI
TI
AI
PI
CO_2-rich flue gas
Controlled and measured variables
- Flowrate
- Temperature
- Pressure
- CO_2 concentration
- NH_3 concentration
TI
LI
FI
TI
Measured variables
- Flowrate
- Temperature
- CO_2 concentration
- NH_3 concentration
FIC
AI
CO_2-rich solution

Pilot test results





82 experimental points



Rate-based model

Experimental value
or
computed by the model

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

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

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*

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

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

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**

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

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

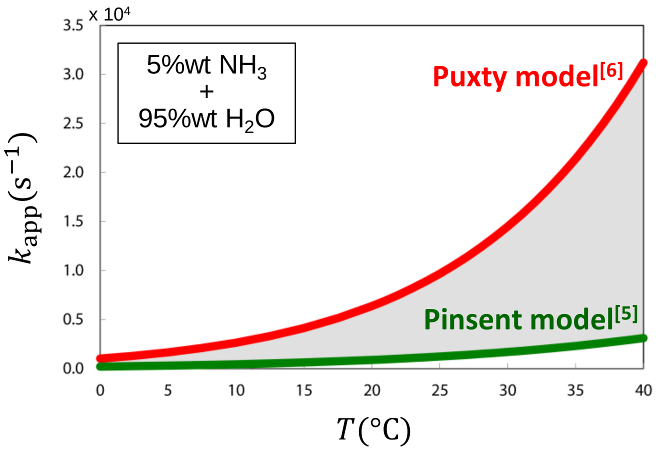
L-phase reaction kinetics – Validation of literature models

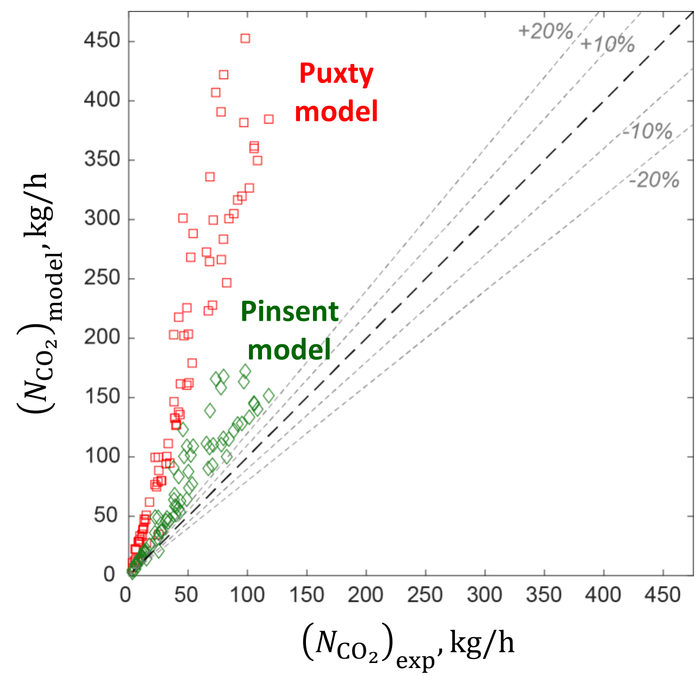
$$\left.\begin{array}{l} \cancel{CO_2 + OH^- \xrightarrow{k_{bc}} HCO_3^-} \\ CO_2 + 2NH_3 \xrightarrow{k_{cm}} NH_2COO^- + NH_4^+ \end{array}\right\}$$

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

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

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





Simple mechanism

$$\left\{\begin{array}{l} CO_2 + NH_3 \rightarrow NH_2COO^- + H^+ \\ NH_3 + H^+ \rightarrow NH_4^+ \end{array}\right.$$

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

[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

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

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

➔ **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

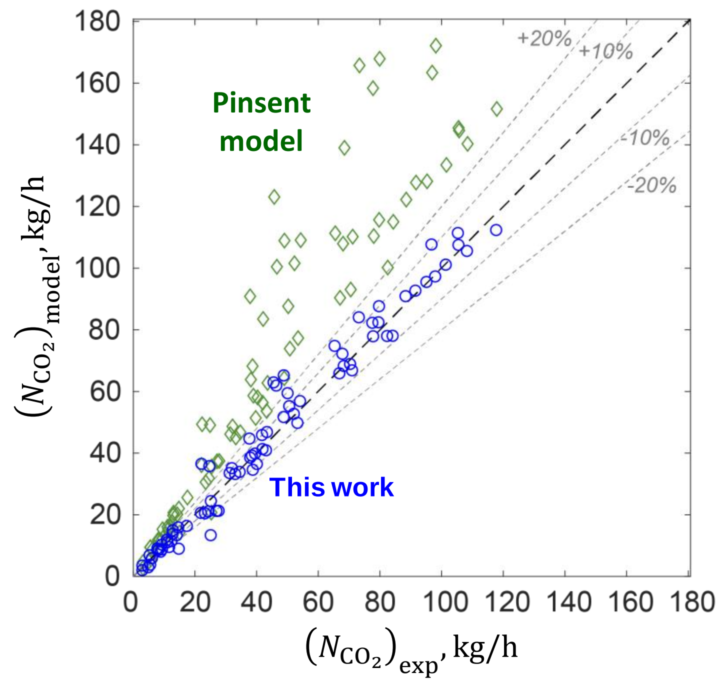
$$\begin{cases} CO_2 + NH_3 \leftrightarrow NH_3^+COO^- \\ NH_3^+COO^- + NH_3 \rightarrow NH_2COO^- + NH_4^+ \\ NH_3^+COO^- + H_2O \rightarrow NH_2COO^- + H_3O^+ \end{cases}$$

Empirical expression

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

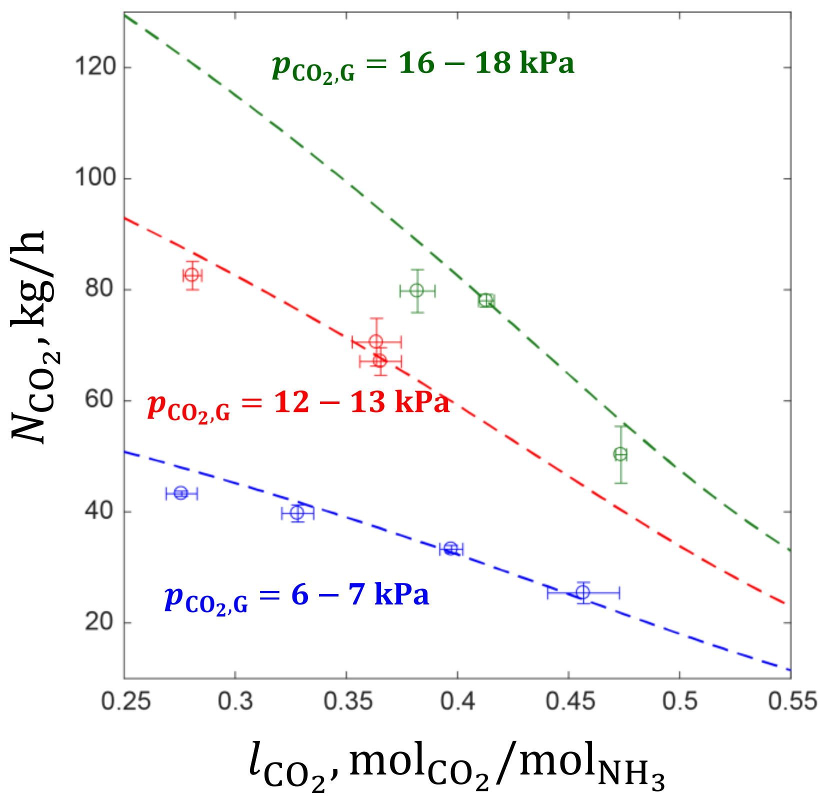
$$1 \leq n \leq 2$$

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



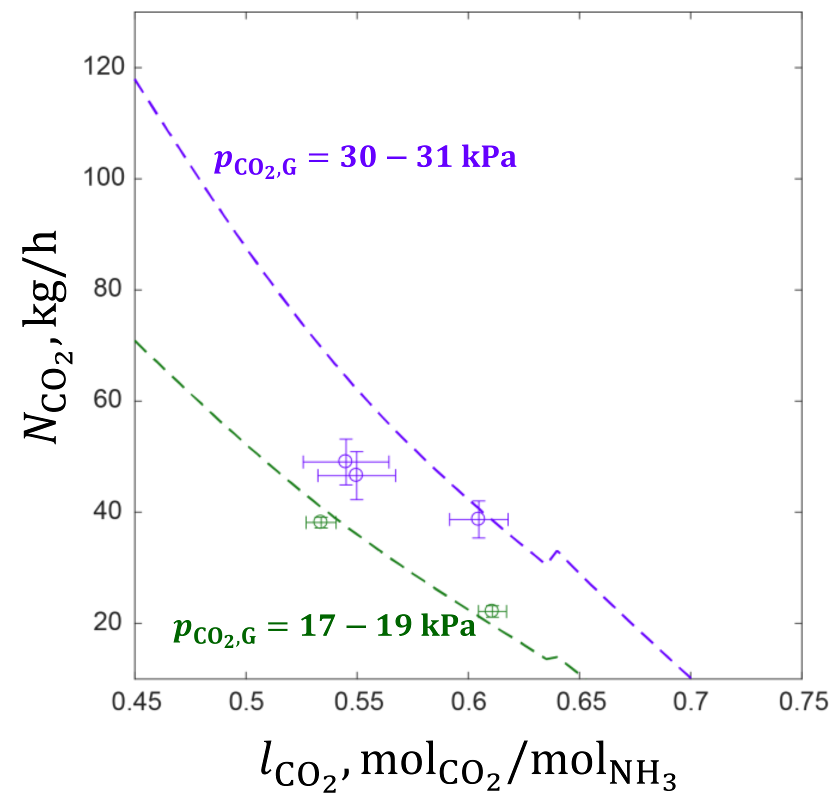
Rate-based model performance assessment (1)

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

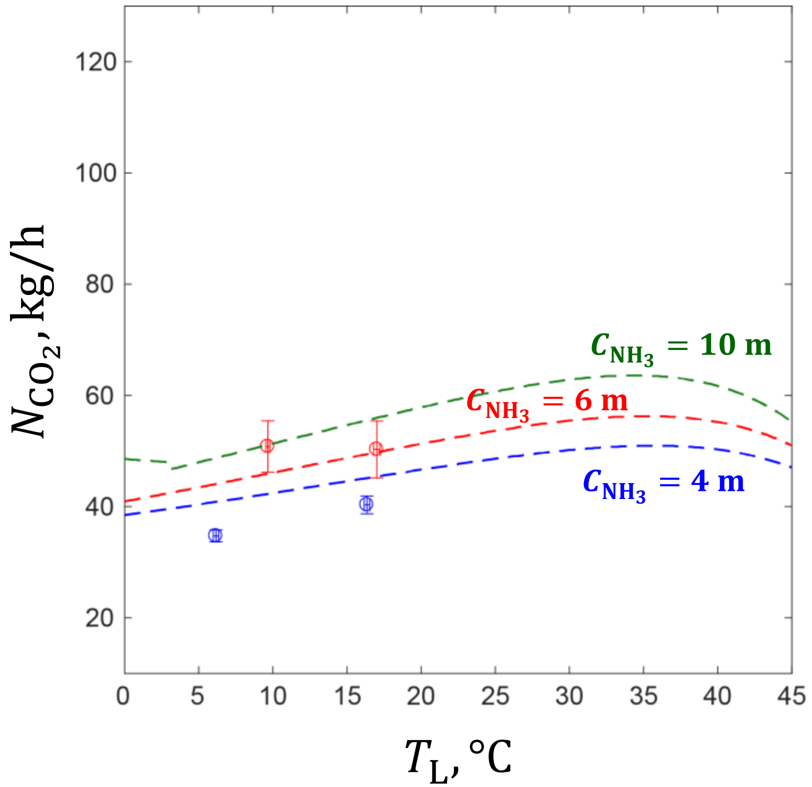
Set B – high CO_2 loading



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

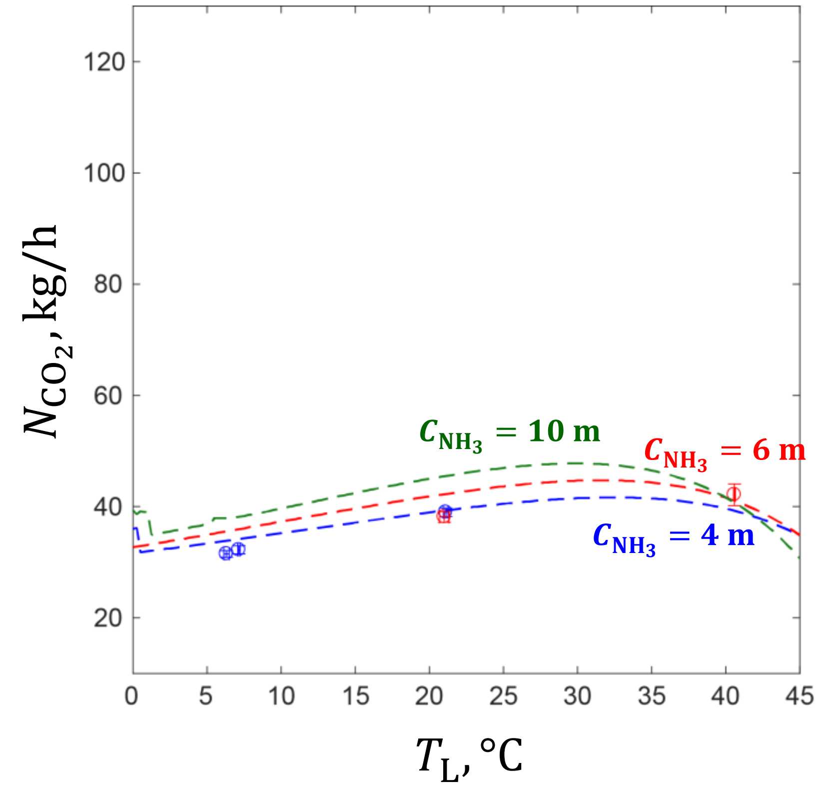
Rate-based model performance assessment (2)

Set C – low CO_2 loading



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

Set D – high CO_2 loading



$p_{CO_2,G} = 17 - 19$ kPa
$l_{CO_2} = 0.52 - 0.54\ \mathrm{mol_{CO_2}/mol_{NH_3}}$
$\frac{L}{G} = 10.7 - 11.4$ 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

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CEMCAP

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