# Application of an aqueous ammonia-based process for $CO_2$ capture to different industrial sources

ETH zürich


José-Francisco Pérez-Calvo, Matteo Gazzani, Daniel Sutter, Federico Milella, Marco Mazzotti

*Institute of Process Engineering, ETH Zurich, CH-8092 Zurich, Switzerland*

*marco.mazzotti@ipe.mavt.ethz.ch*


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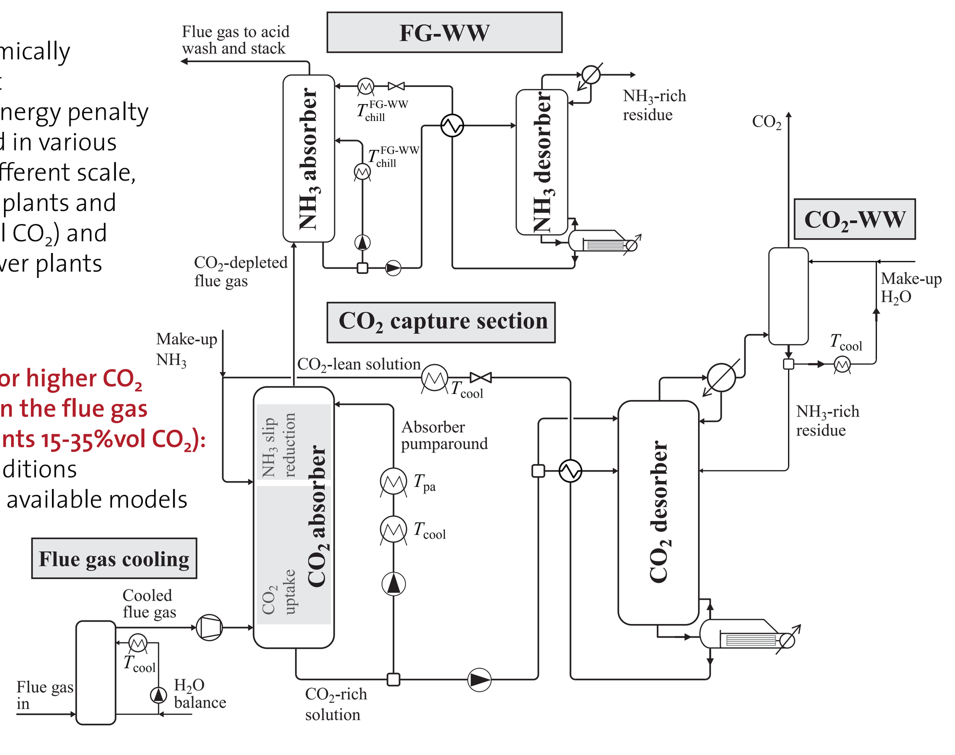
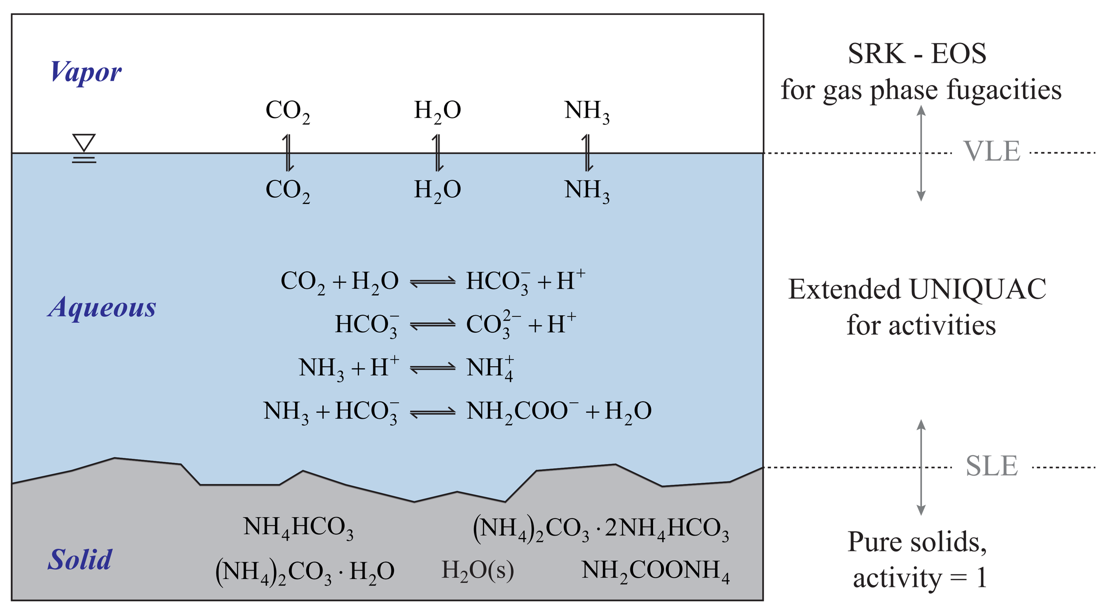
## 1. Chilled Ammonia Process

**Features:**
- low-cost, chemically stable solvent
- competitive energy penalty
- demonstrated in various facilities of different scale, i.e. NG power plants and cracker (4%vol $CO_2$) and coal-fired power plants (14%vol $CO_2$)

**Uncertainties for higher $CO_2$ concentration in the flue gas (i.e. cement plants 15-35%vol $CO_2$):**
- operating conditions
- validity of the available models

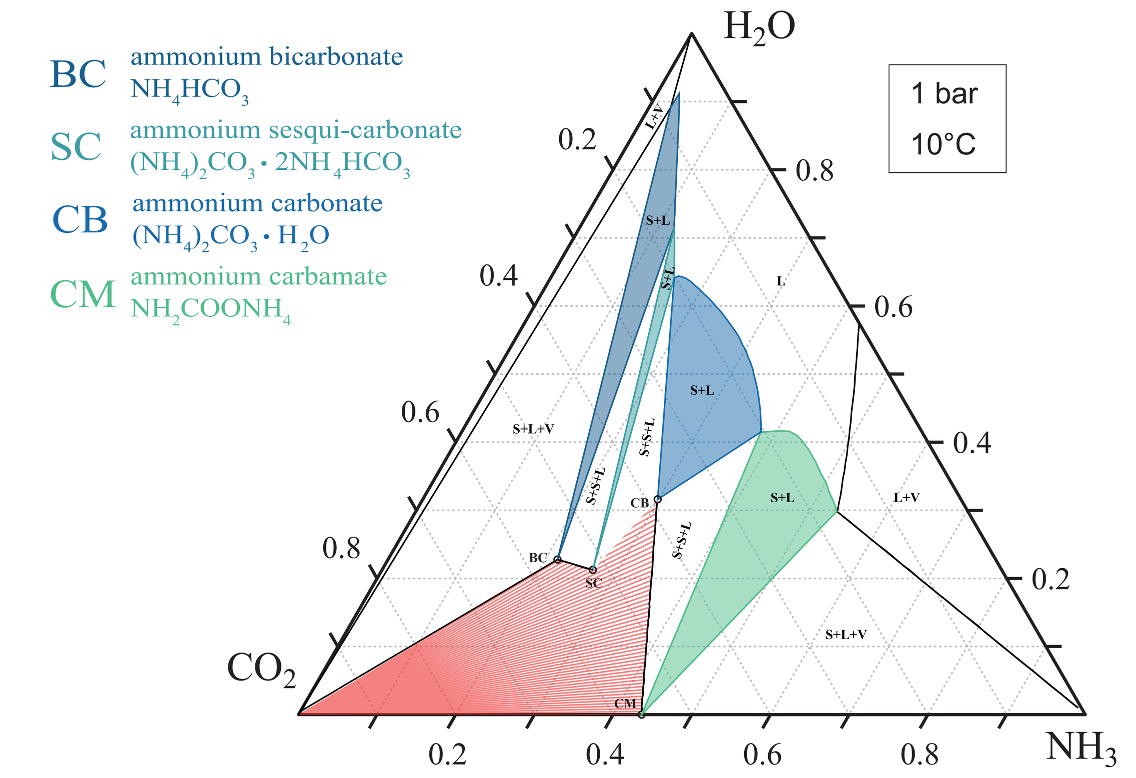



## 2. The $CO_2$-$NH_3$-$H_2O$ system

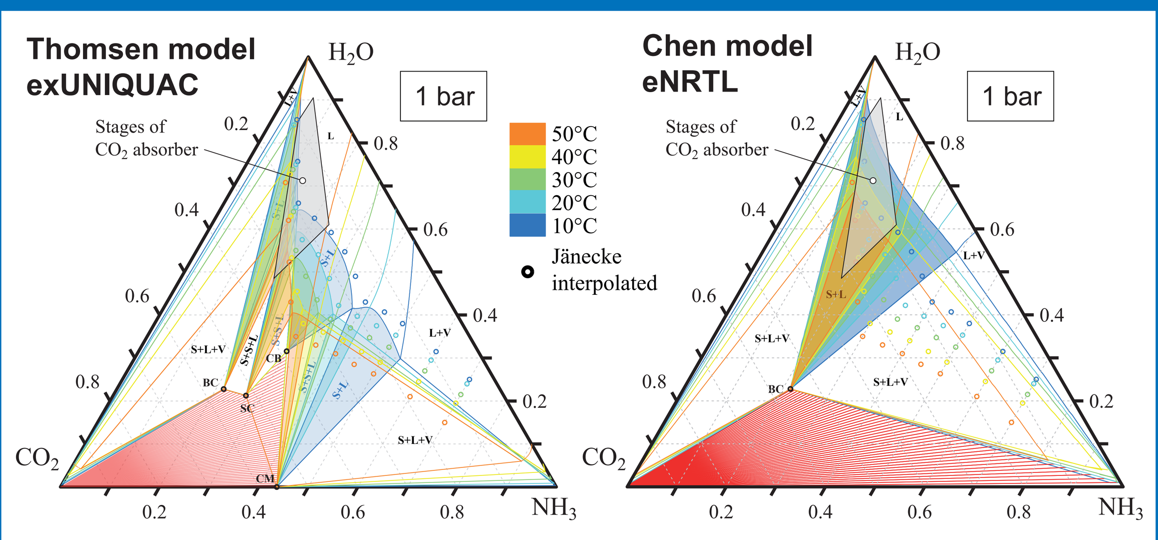



- **Thermodynamic model** developed by Thomsen et al. (1999) and Darde et al. (2010)
- Solid properties based on Jänecke (1929)

## 3. Phase diagrams




## 4. Thermodynamic model




## 5. Rate-based model

Aspen Plus RadFrac distillation model (RateSep)

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

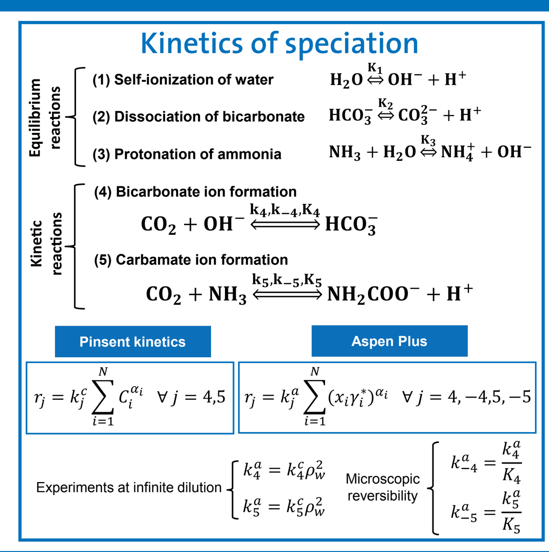
$K_{G,CO_2} = f$ (physical mass transfer, L-phase reaction kinetics) — Correlations and numerical options available in Aspen Plus

$A_{int} = f$(hydrodynamics)

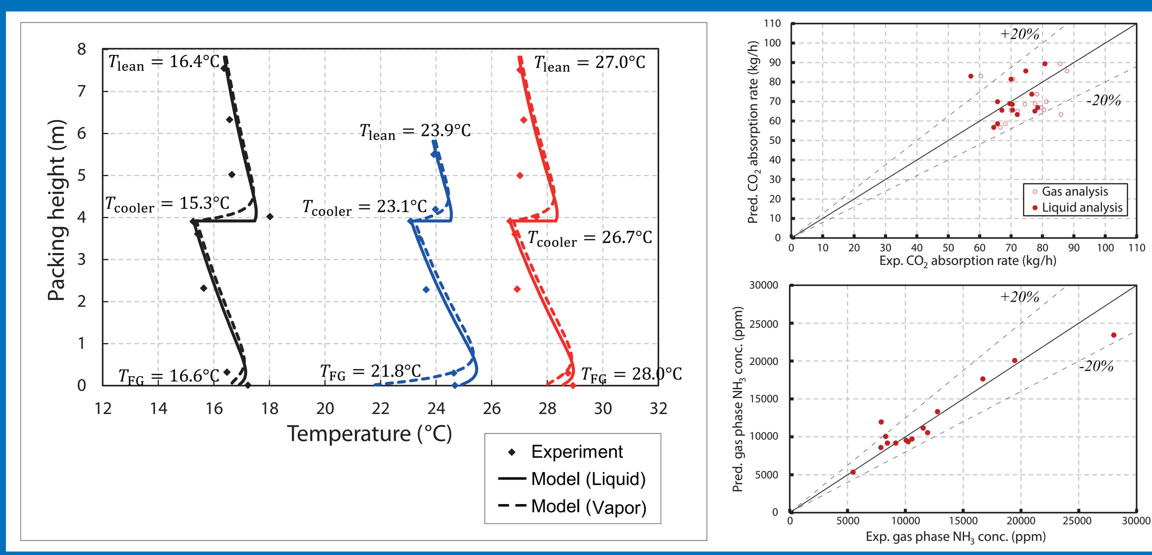
$(P_{CO_2} - P^*_{CO_2}) = f$(thermodynamics)

This work:

**Thomsen** thermodynamic **model** to compute the **driving force** instead of Chen thermodynamic model as generally done in the literature.

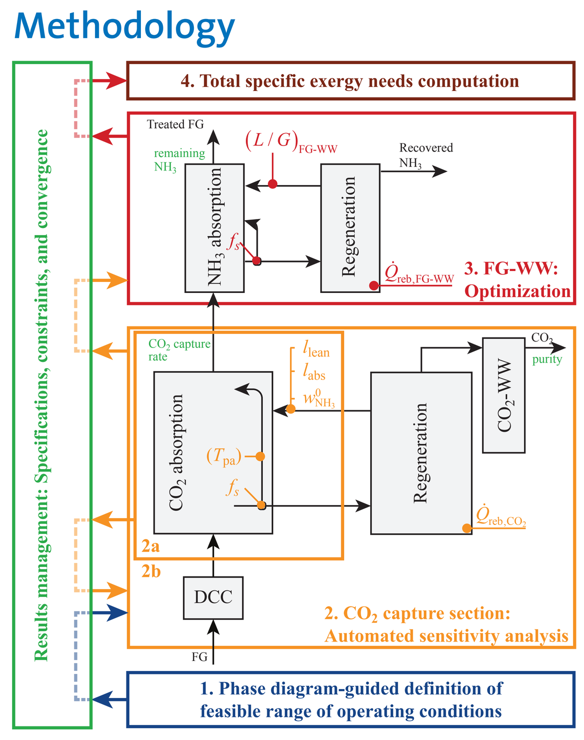



## 6. Model validation (CSIRO tests)




## 7. Heuristic process optimization

### Methodology




### Objective function

**Total Specific Exergy Needs**

$$w = \frac{W_{\text{reboilers}} + W_{\text{chilling}} + W_{\text{auxiliaries}}}{m^{\text{capt}}_{CO_2}} \left[\frac{\text{MJ}}{\text{kg } CO_2 \text{ captured}}\right]$$

**Reboilers**

$$W_{\text{reboilers}} = \dot{Q}_{\text{reb},CO_2}\left(1 - \frac{T_{\text{amb}}}{T_{\text{reb},CO_2} + \Delta T_{\min}}\right) + \dot{Q}_{\text{reb,FG-WW}}\left(1 - \frac{T_{\text{amb}}}{T_{\text{reb,FG-WW}} + \Delta T_{\min}}\right)$$

**Chilling**

$$W_{\text{chilling}} = \frac{\dot{Q}_{\text{chilling}}}{\text{COP}} \qquad \text{COP} = \text{COP}_{\text{ideal}} \cdot \eta_r \qquad \text{COP}_{\text{ideal}} = \frac{T_{\text{cold}}}{T_{\text{hot}} - T_{\text{cold}}}$$

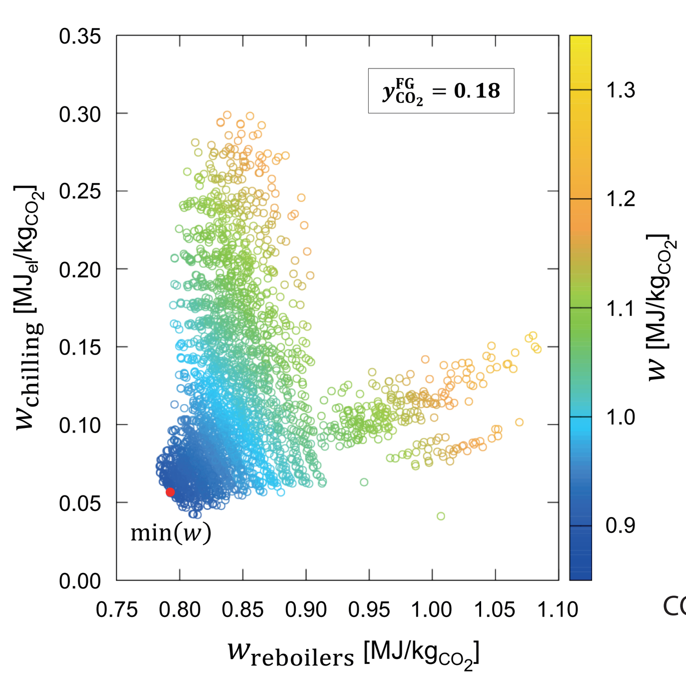
**Auxiliaries**

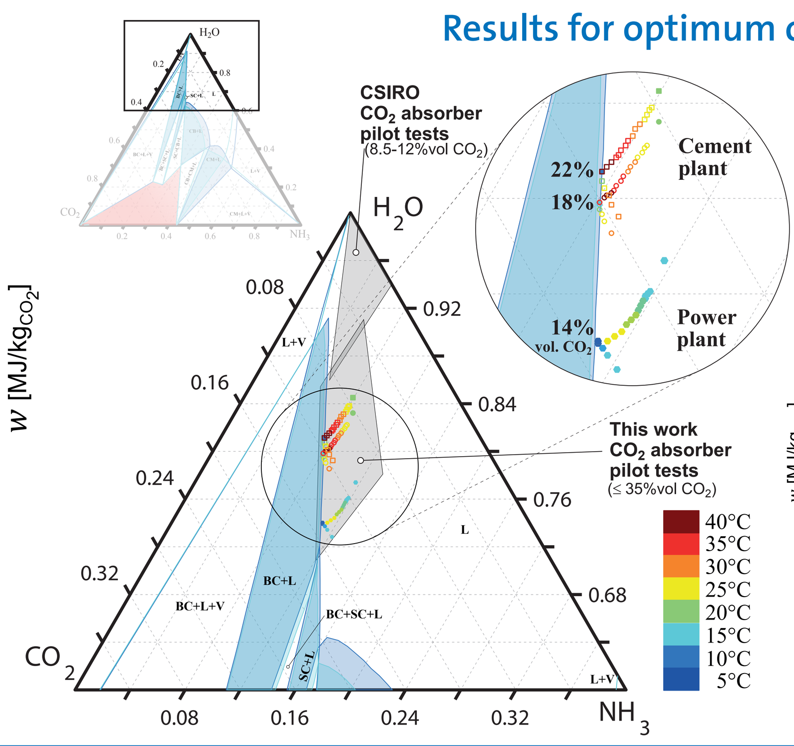
$$W_{\text{auxiliaries}} = \frac{W_{\text{ideal}}}{\eta_{\text{pump}}}$$

### Specifications and constraints

- $CO_2$ capture > 85%
- $CO_2$ purity > 95%mole
- $NH_3$ slip < 200 ppm
- No solid formation

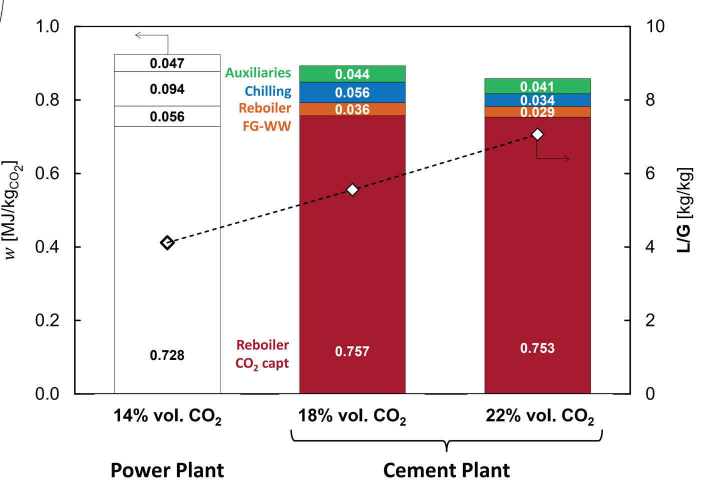
### Heuristic optimization results



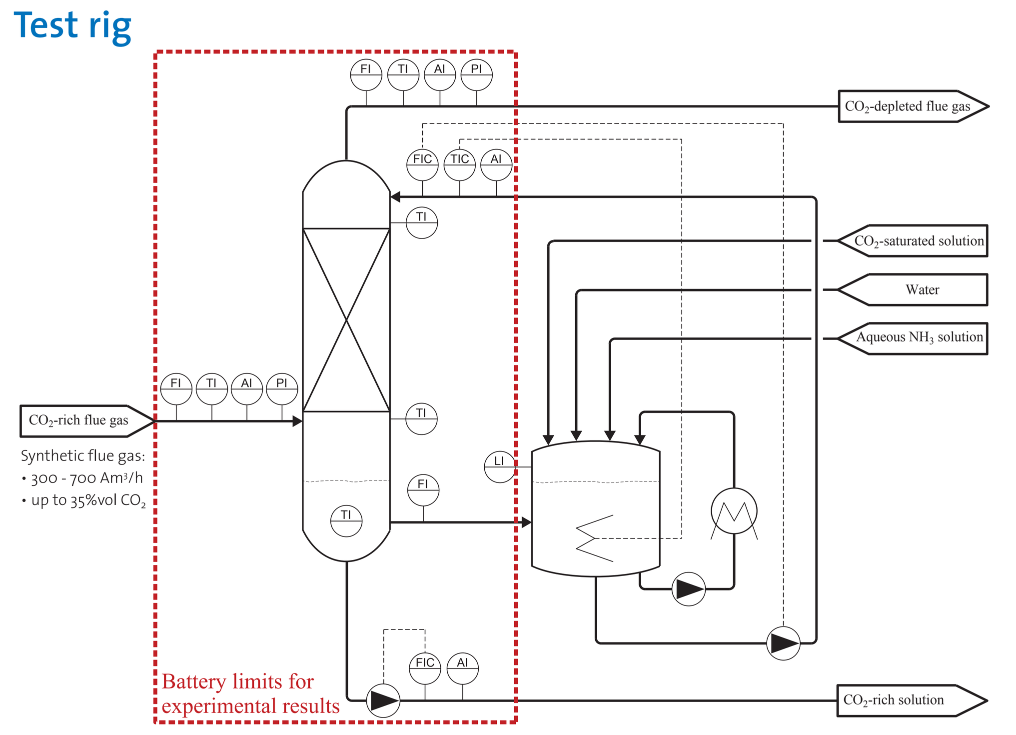

### Results for optimum operating conditions

Higher $CO_2$ concentration in the flue gas leads to:
- Lower specific exergy needs
- Increase in the liquid $CO_2$-lean to flue gas flowrate ratio
- Decrease in the $NH_3$ content of the $CO_2$-lean stream
- Approximately constant $CO_2$ loading in the $CO_2$-lean stream




## 8. Pilot tests for $CO_2$ absorber

### Test rig

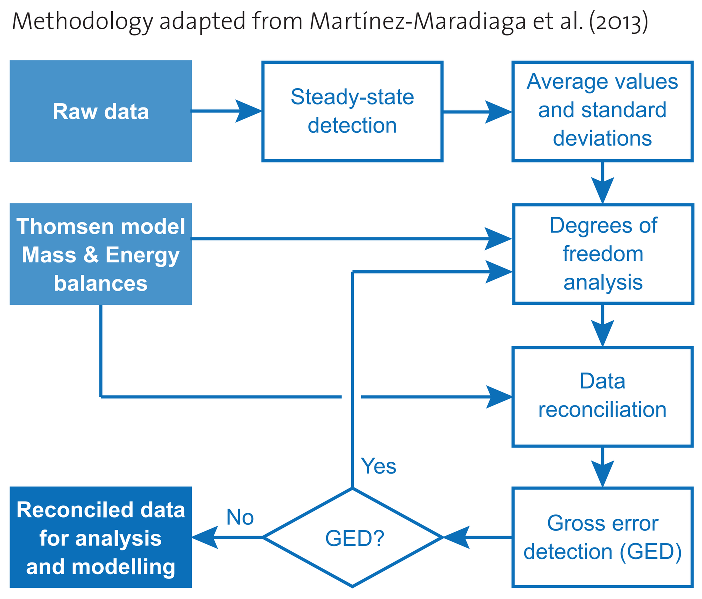



### Experimental matrix

76 experiments performed:
- $CO_2$ capture and $NH_3$ removal tests
- Test the $CO_2$ absorber model at extreme conditions
- Sensitivity analysis ($y^{\text{in}}_{CO_2}, l^{\text{in}}_{CO_2}, m^{\text{in}}_{NH_3}, T^{\text{in}}_L, L^{\text{in}}/G^{\text{in}}, v^G_S$)
- Repeatability of experiments

### Systematic treatment of raw pilot data

Methodology adapted from Martinez-Maradiaga et al. (2013)




### Initial Degrees of Freedom (DoF) analysis

**#Equations = 11**
- 1 x Total mass balance
- 3 x Component mass balances
- 1 x Energy balance
- 4 x Stoichiometric equations
- 2 x Gas streams saturated in $H_2O$

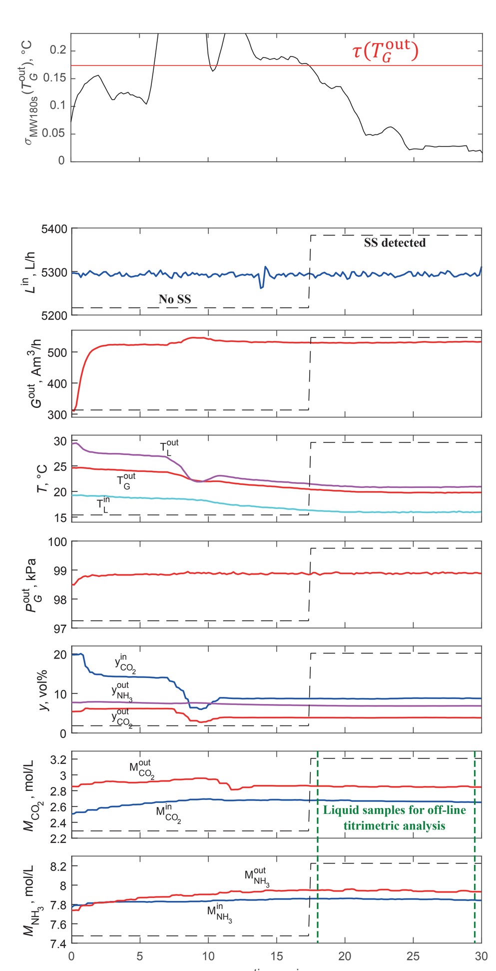
**#Unknowns = 6**
- $x^{\text{in}}_{H_2O}, x^{\text{out}}_{H_2O}, y^{\text{in}}_{H_2O}, y^{\text{out}}_{H_2O}, y^{\text{in}}_{\text{air}}, y^{\text{out}}_{\text{air}}$

**DoF = 6 - 11 = -5**
- Overdeterminded system
- Up to 5 measured variables could be overlooked

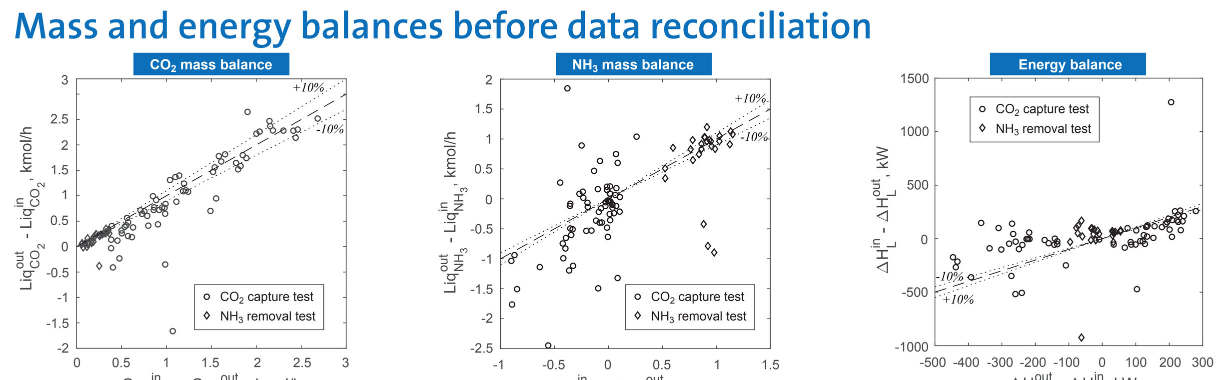
### Steady-state (SS) detection

Methodology based on a moving window (Kim et al., 2008):
- Representative SS period to compute standard deviations $(\sigma(u_i^{\text{ref}}))$
- Sensitivity analysis to select:
  - Moving window size: $\text{MW} = 180\ \text{s}$
  - Threshold for each measured variable: $\tau(u_i) = \lambda_i\, \sigma(u_i^{\text{ref}})$ with $\lambda_i = 1, 2, 3$
- SS detection if

$$\sigma_{\text{MW180s}}(u_{i^*}) \le \tau(u_{i^*}) \quad \forall\, i^*$$




### Mass and energy balances before data reconciliation



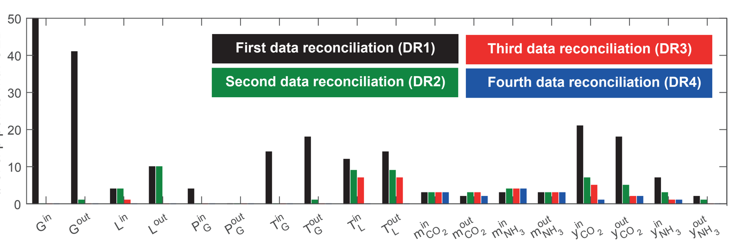

### Data reconciliation (DR)

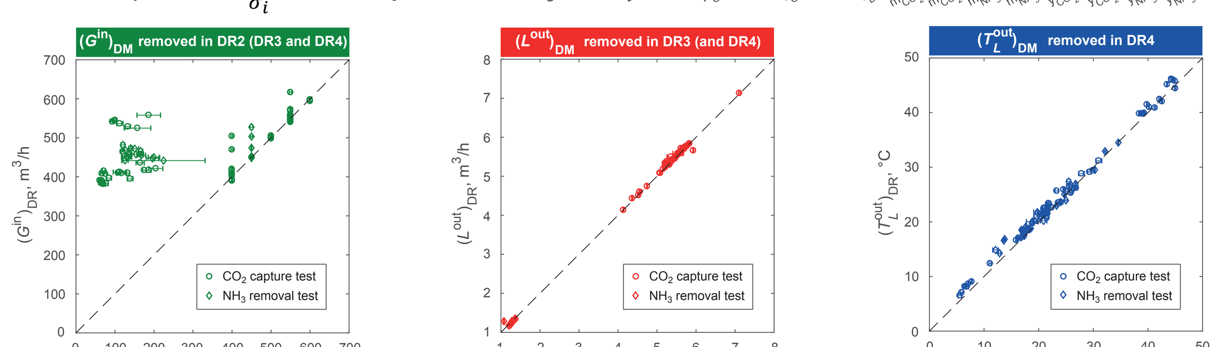
$$F = \min \sum_i \left(\frac{(u_i)_{\text{DR}} - (u_i)_{\text{DM}}}{\sigma_i}\right)^2$$

subjected to:

$\overline{f}(\overline{u_{DR}}, \overline{z}) = 0$
- Total, $CO_2$, $NH_3$ and air mass balances
- Energy balance

- GED if $e_i = \frac{|(u_i)_{\text{DR}} - (u_i)_{\text{DM}}|}{\sigma_i} \ge e_c$

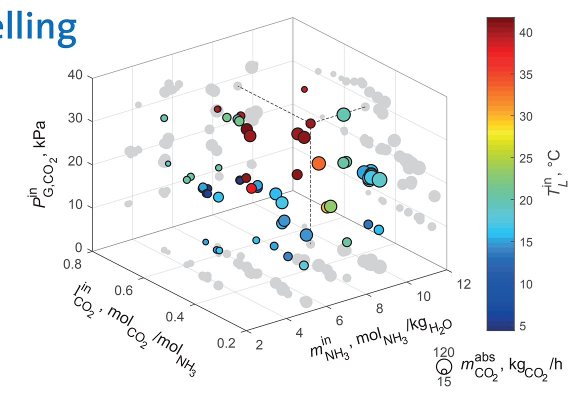



### Reconciled data for analysis and modelling

**76 experiments performed at pilot plant scale**
- From SS detection: 89 experimental points
  - No SS detected: 3 experiments
  - 2 different SS periods detected: 16 experiments
- After DR4 and GED: 82 experimental points
  - GED in liquid and/or gas measured composition: 7 experimental points discarded

**82 experimental points for analysis and modelling**
- 60 points testing $CO_2$ capture (see plot on the right)
- 22 points testing $NH_3$ removal



## 9. Summary and conclusions

- The Chilled Ammonia Process can be applied for $CO_2$ capture to different industrial sources.
- A rate-based model using the Thomsen thermodynamic model has been validated with pilot tests from literature.
- The heuristic optimization approach has led to the optimum set of operating conditions of the process, based on:
  - The exergy requirements as the objective function.
  - Equilibrium model using the Thomsen thermodynamic model with ad-hoc Murphree efficiencies for cement plant flue gas compositions.
- $CO_2$ absorber tests mimicking power plant and cement plant-like flue gas compositions have been performed.
- A systematic procedure for the post-treatment of the raw pilot plant data has been developed.
  - Data reconciliation and gross error detection allowed to detect malfunctioning instruments and deceptive measurements and to discard unreliable experimental points.
  - Reconciled data constrained to the fulfillment of the mass and energy balances will be used for the analysis of the experimental results in terms of $CO_2$ capture rate and $NH_3$ removal efficiency and for further rate-based model development.

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