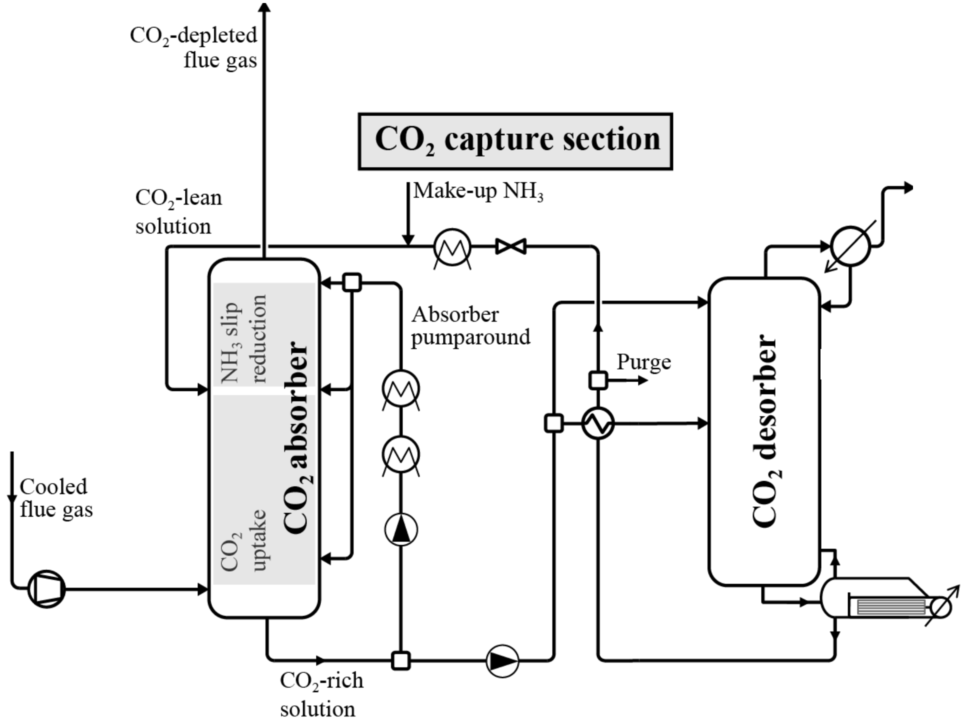
José-Francisco Pérez-Calvo, Daniel Sutter, Matteo Gazzani and Marco Mazzotti

Simulation, modelling and optimization of different chilled ammonia-based process configurations for CO_2 capture applied to cement plants

The CAP



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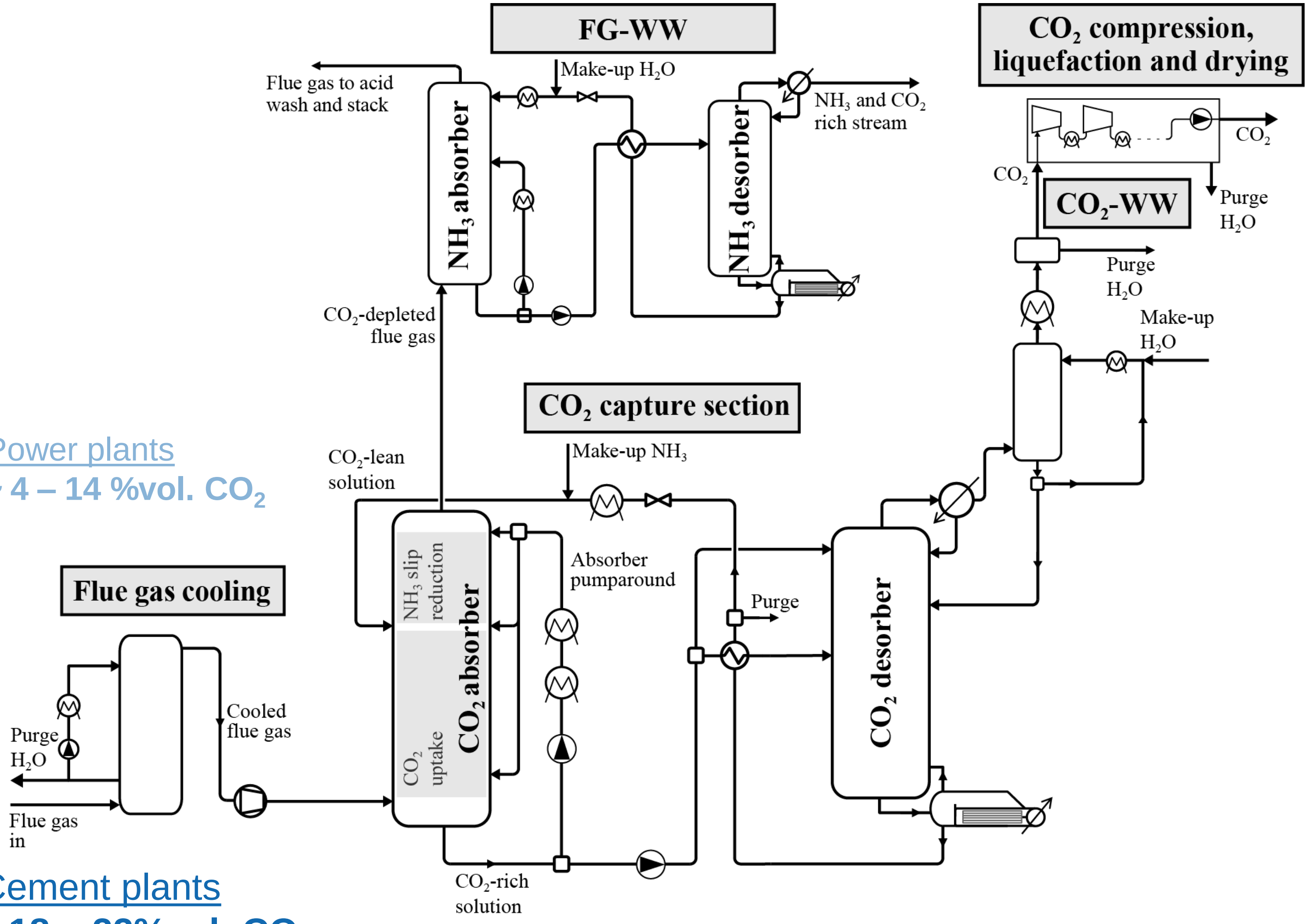
From power to cement plants



Power plants
~ 4 – 14 %vol. CO_2

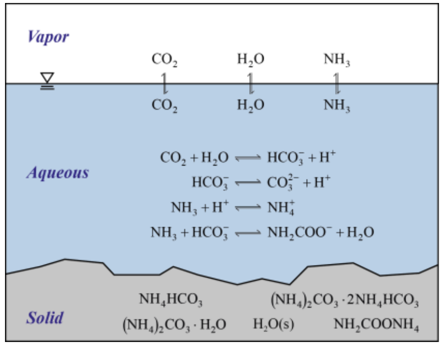
Cement plants
~ 18 – 22%vol. CO_2

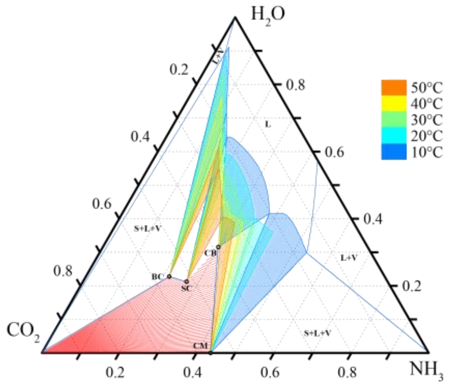
SCOPE OF THE STUDY

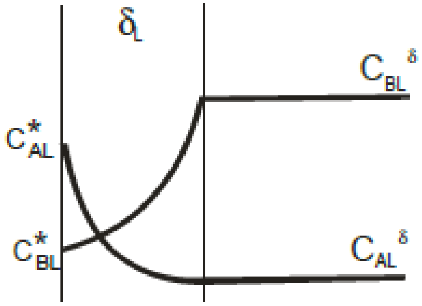
- To adapt the CAP to cement plants for CO_2 capture
- To prove that the higher CO_2 concentration in the flue gas improves the performance of the CAP
- To show that the CAP has better performance than MEA-based processes for CO_2 capture from cement plants

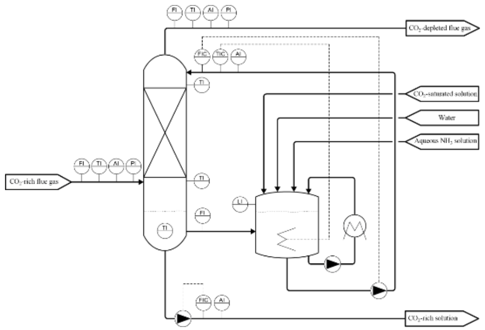
Holistic process development

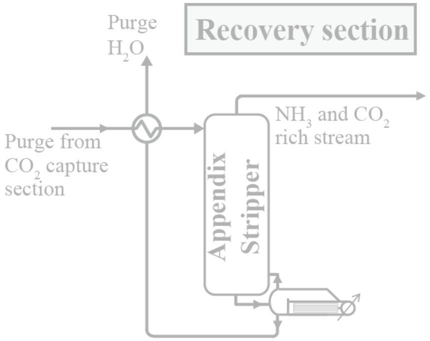
Rate-based model development		Model-based process design and development		
Thermodynamics	Trans Phenom & Kin	Synthesis	Optimization	Integration

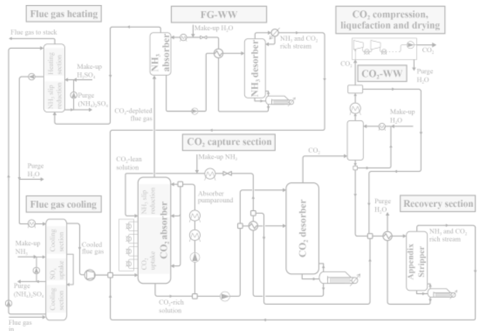


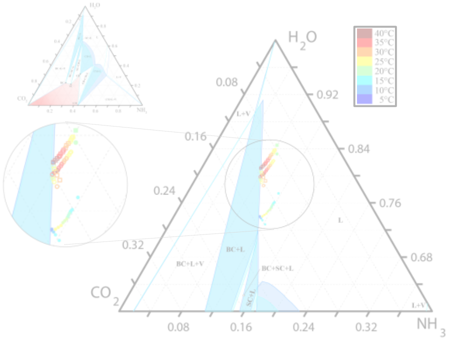


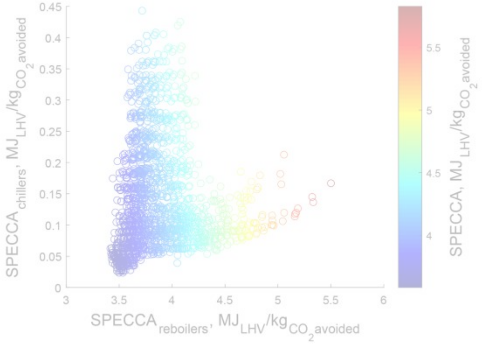


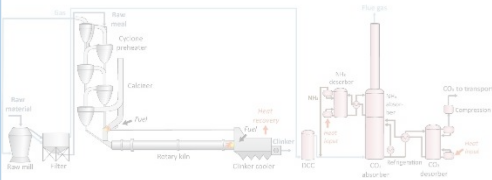


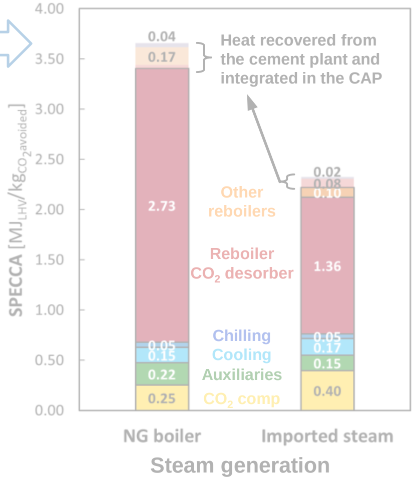












Rate-based model

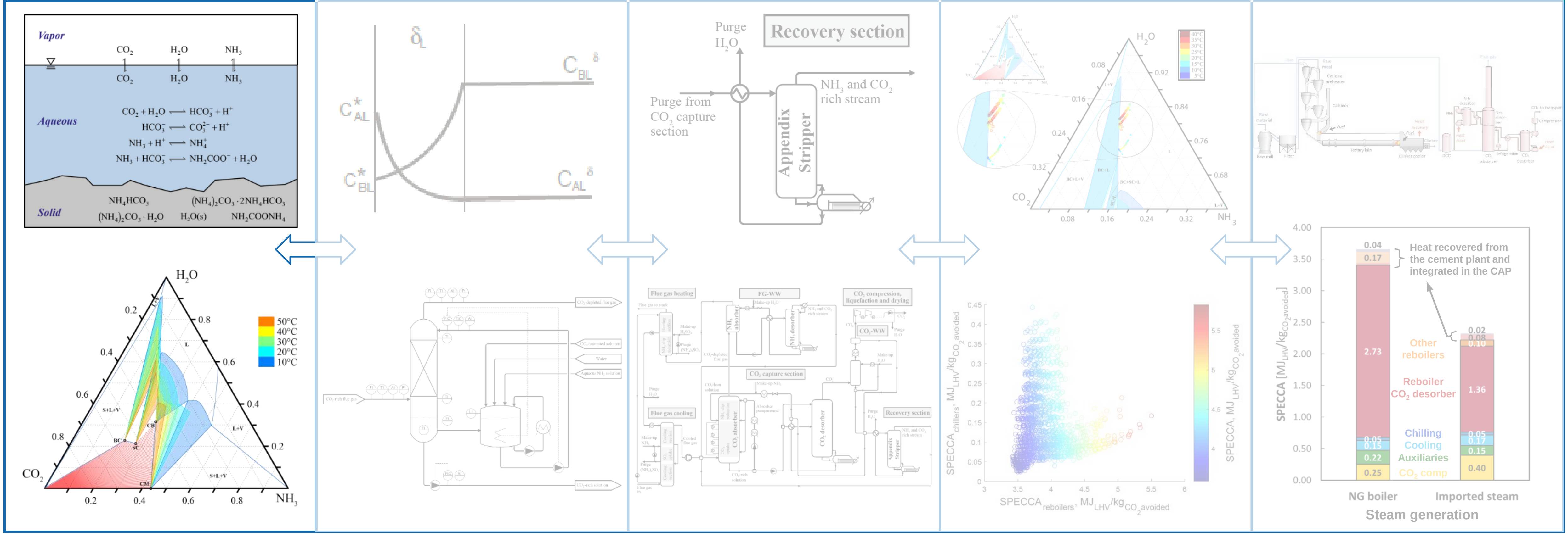
Aspen Plus RadFrac distillation model (RateSep)

Simplifying: $N_{CO_2} = A_{eff} K_{G,CO_2} \left(p_{CO_2,G} - p^*_{CO_2,L}\right)$, with $\frac{1}{K_{G,CO_2}} = \frac{RT}{k_{g,CO_2}} + \frac{H_{CO_2}}{E k^0_{l,CO_2}}$

Phase equilibria	**Thomsen model**	✓ *Predicts SLE in addition to VLE*

Holistic process development

Rate-based model development		Model-based process design and development		
Thermodynamics[1,2]	Trans Phenom & Kin	Synthesis	Optimization	Integration



[1] Darde et al. *Ind Eng Chem Res* 49 (2010) 12663-74
[2] Sutter et al. *Chem Eng Sci* 133 (2015) 170-180

Rate-based model

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Phase equilibria	**Thomsen model**	✓ *Predicts SLE in addition to VLE*
Transport phenomena	**Rochelle model** [1] Wang et al. *Ind Eng Chem Res* 55 (2016) 5357-84	✓ *Range of structured packings: X, Y, Z, 150-350* ✓ *Aqueous solutions for CO_2 capture*
Reaction kinetics	**This work** [2] Pérez-Calvo et al. *Chem Eng Trans* 69 (in press)	✓ *CO_2 absorption pilot plant tests* ✓ *Commercial structured packing* ✓ *Synthetic flue gases containing up to 35%vol CO_2* ✓ *Aqueous ammonia solutions containing up to 17%wt NH_3*

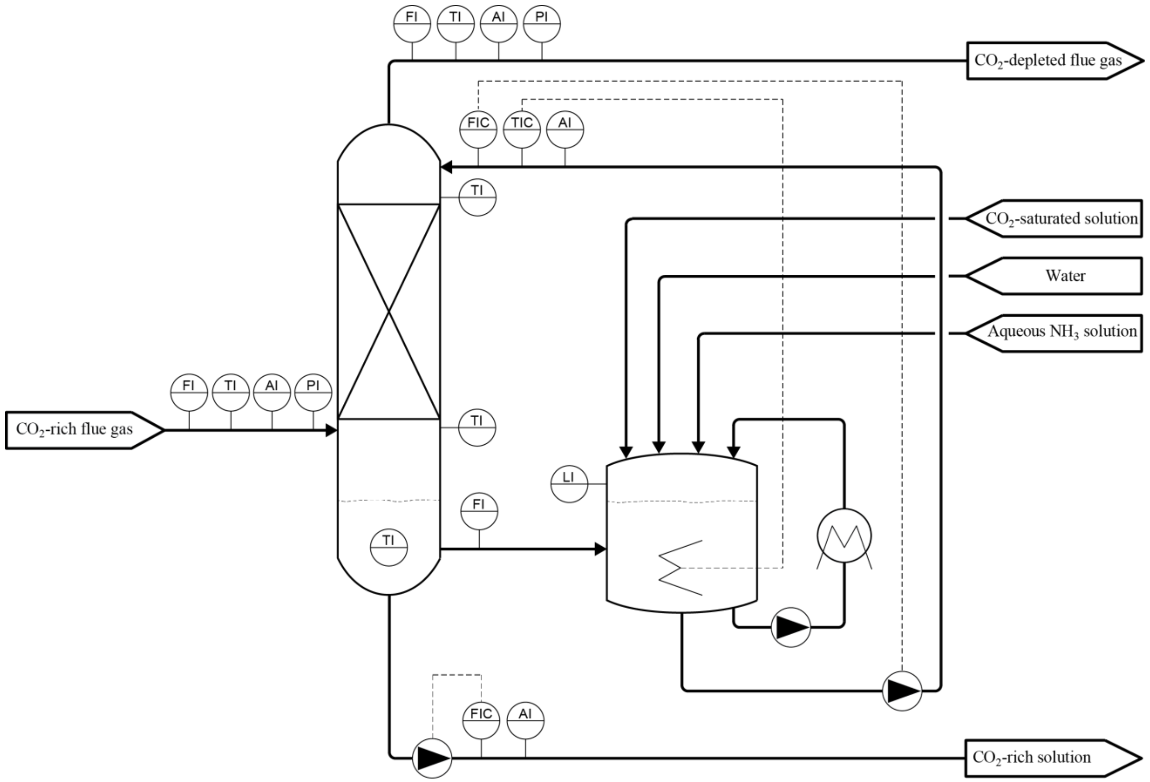
Reaction kinetics – Model fitting

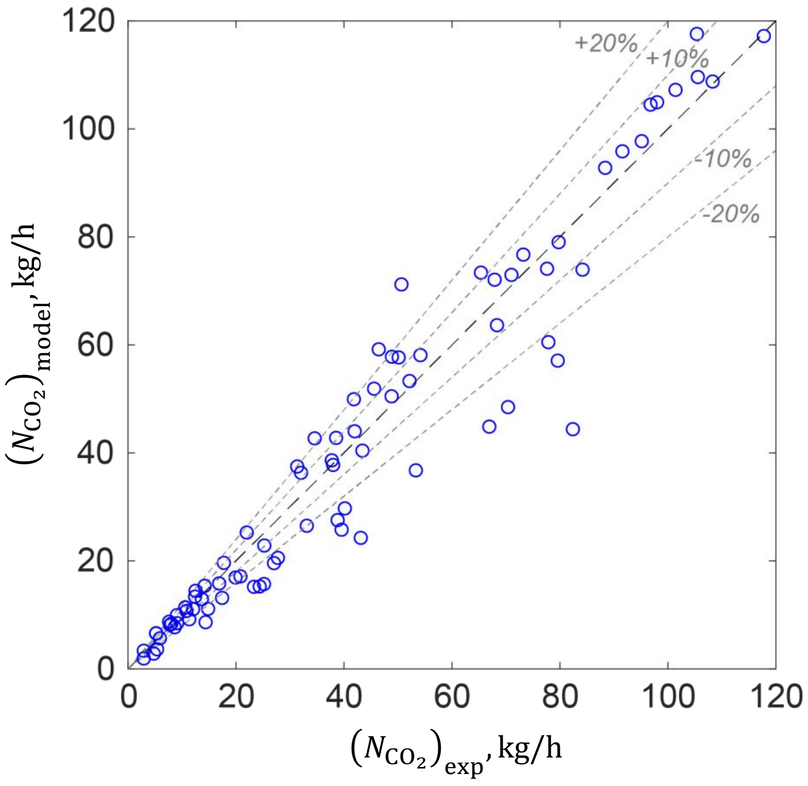
$$CO_2 + 2NH_3 \xrightarrow{k_{cm}} NH_2COO^- + NH_4^+$$

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

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

82 experimental points





Pérez-Calvo et al. *Chem Eng Trans* 69 (in press)

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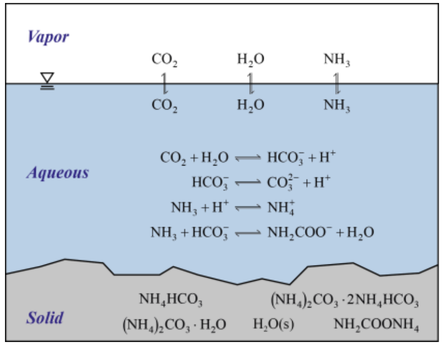
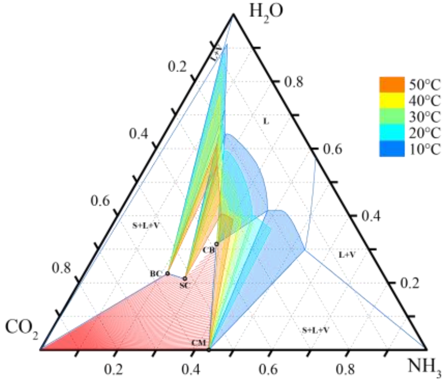
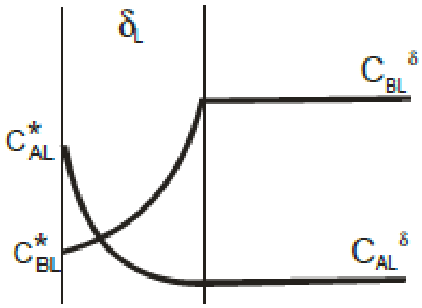
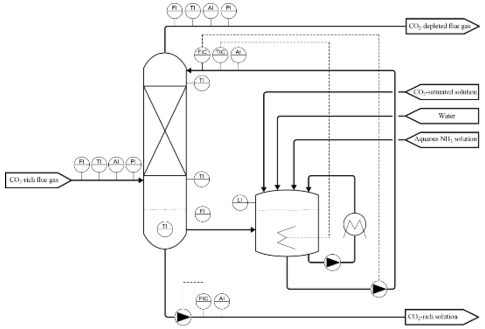
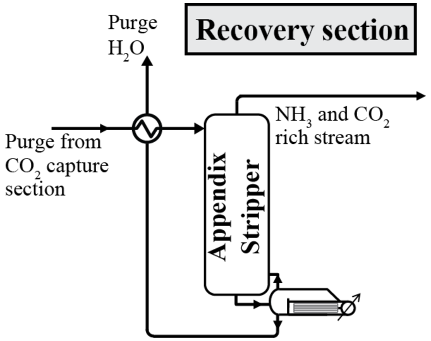
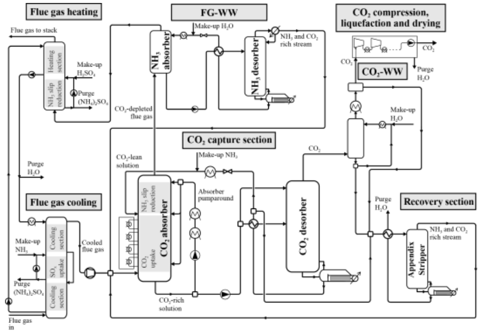


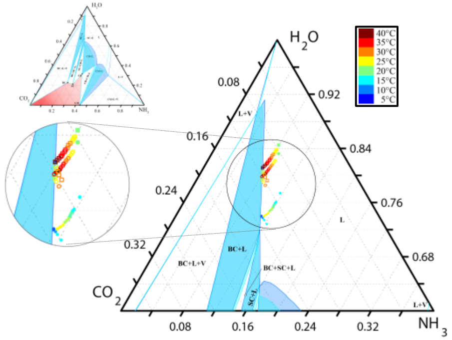


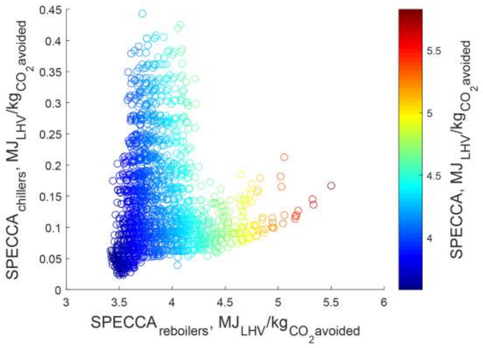


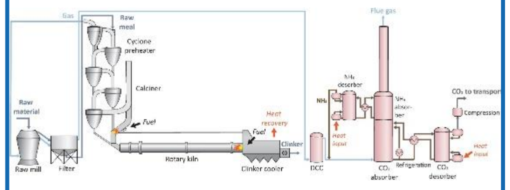


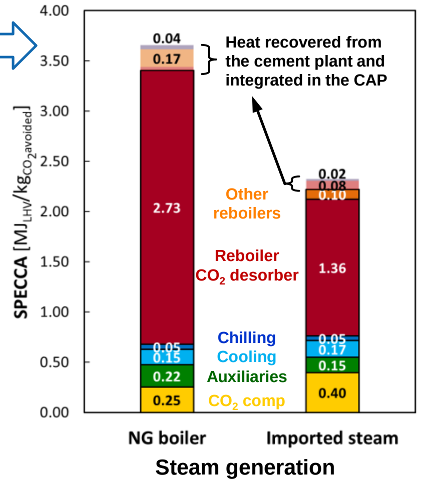




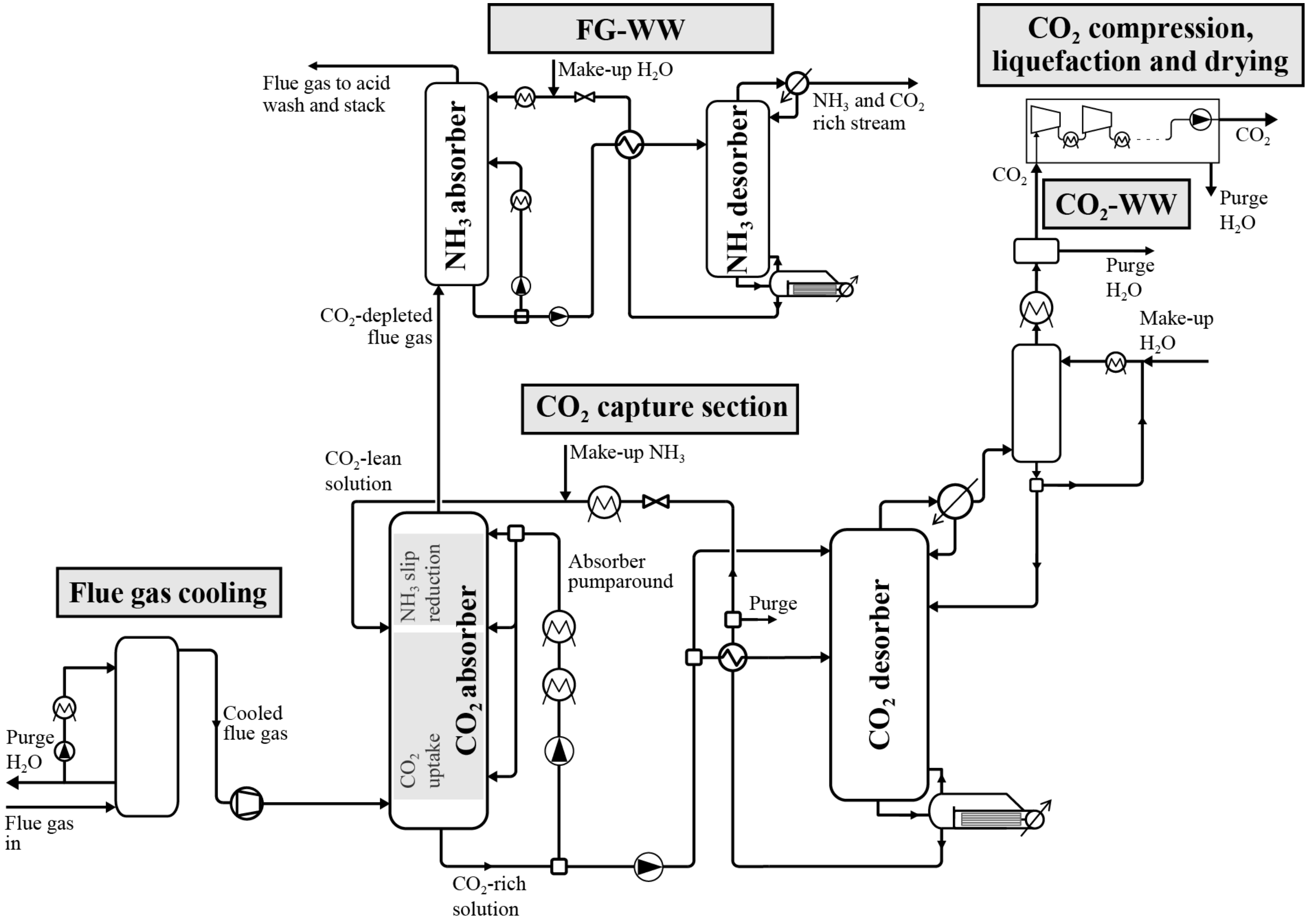








Process synthesis – Towards the CAP for cement application

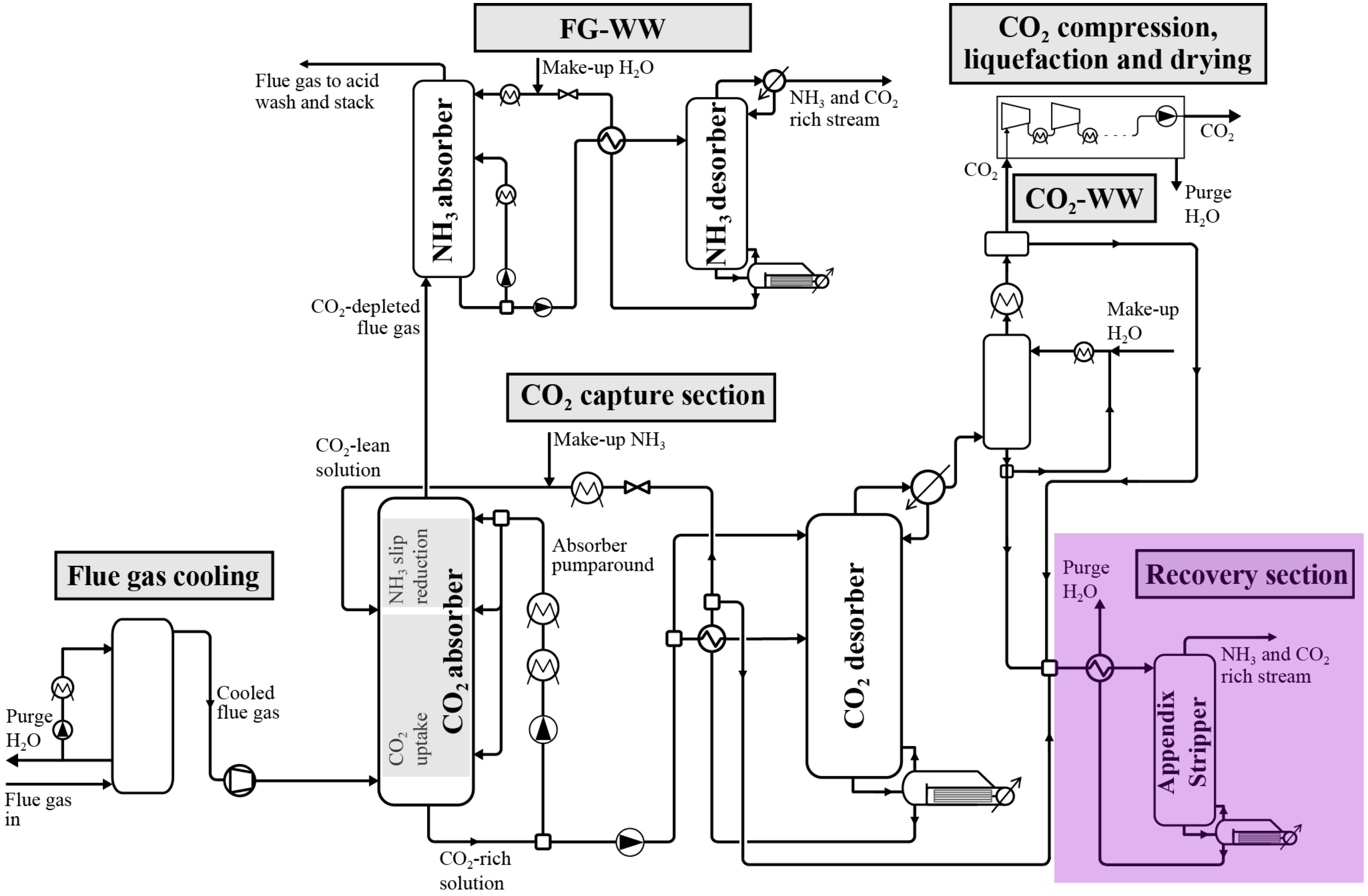


Sutter et al. *Faraday Discuss* 192 (2016) 59-83

General modifications/improvements

1. Decreasing energy consumption
2. Minimizing solvent make-up
3. Decreasing CAPEX
4. Meeting specifications and constraints
5. Avoiding solid formation

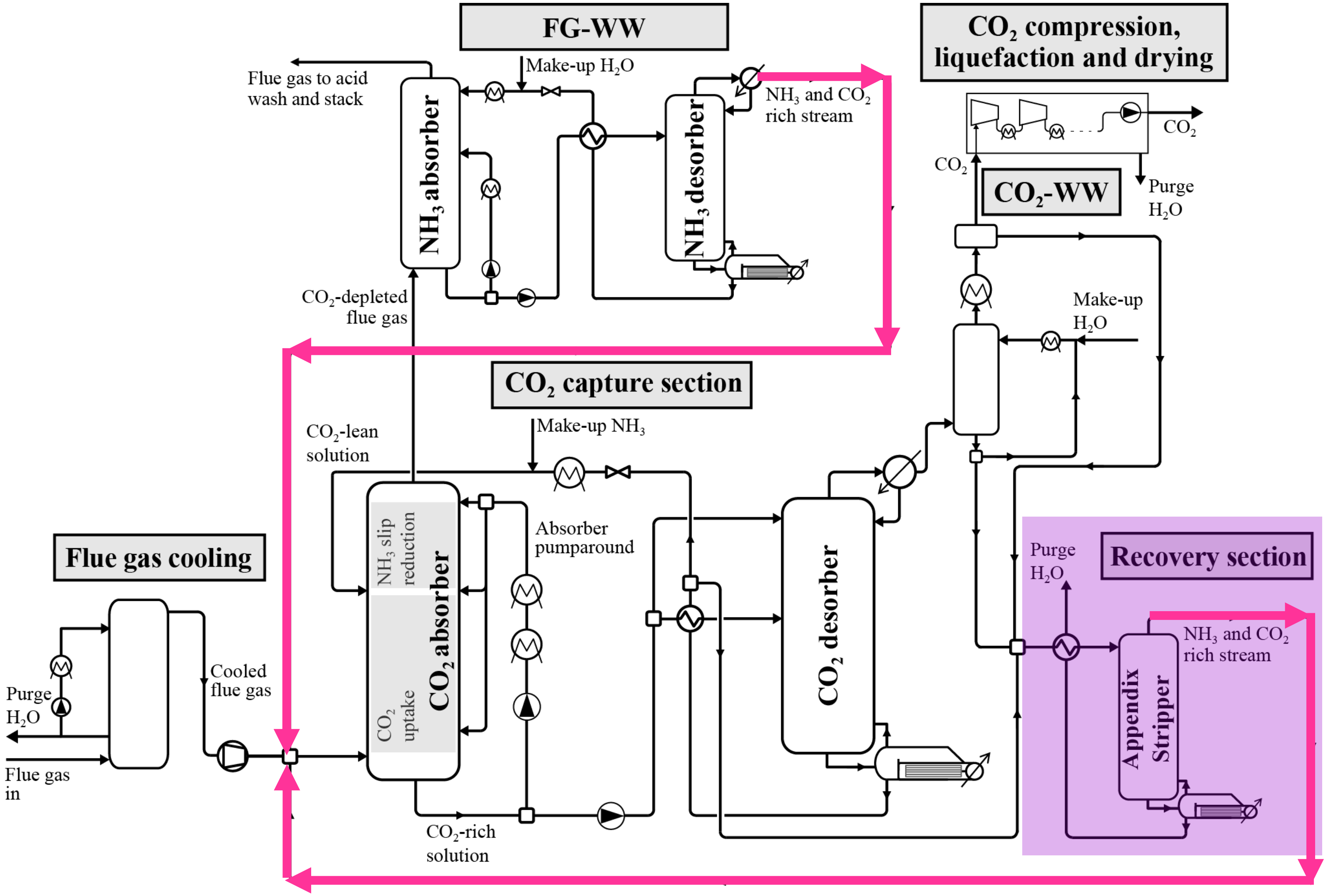
Process synthesis – Towards the CAP for cement application



General modifications/improvements

Solvent recovery section

Process synthesis – Towards the CAP for cement application

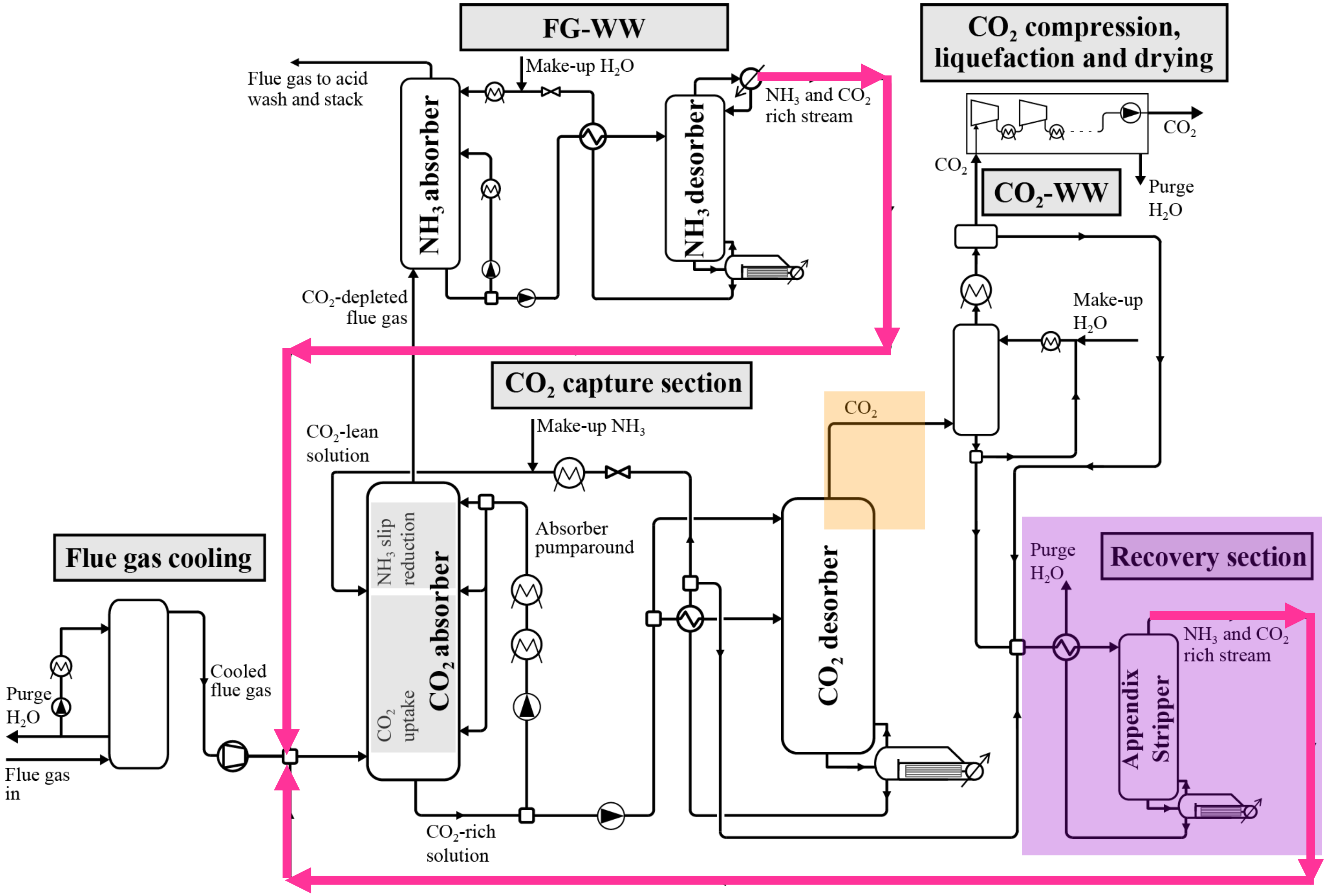


General modifications/improvements

Solvent recovery section

Recycle of the NH_3 and CO_2 rich streams

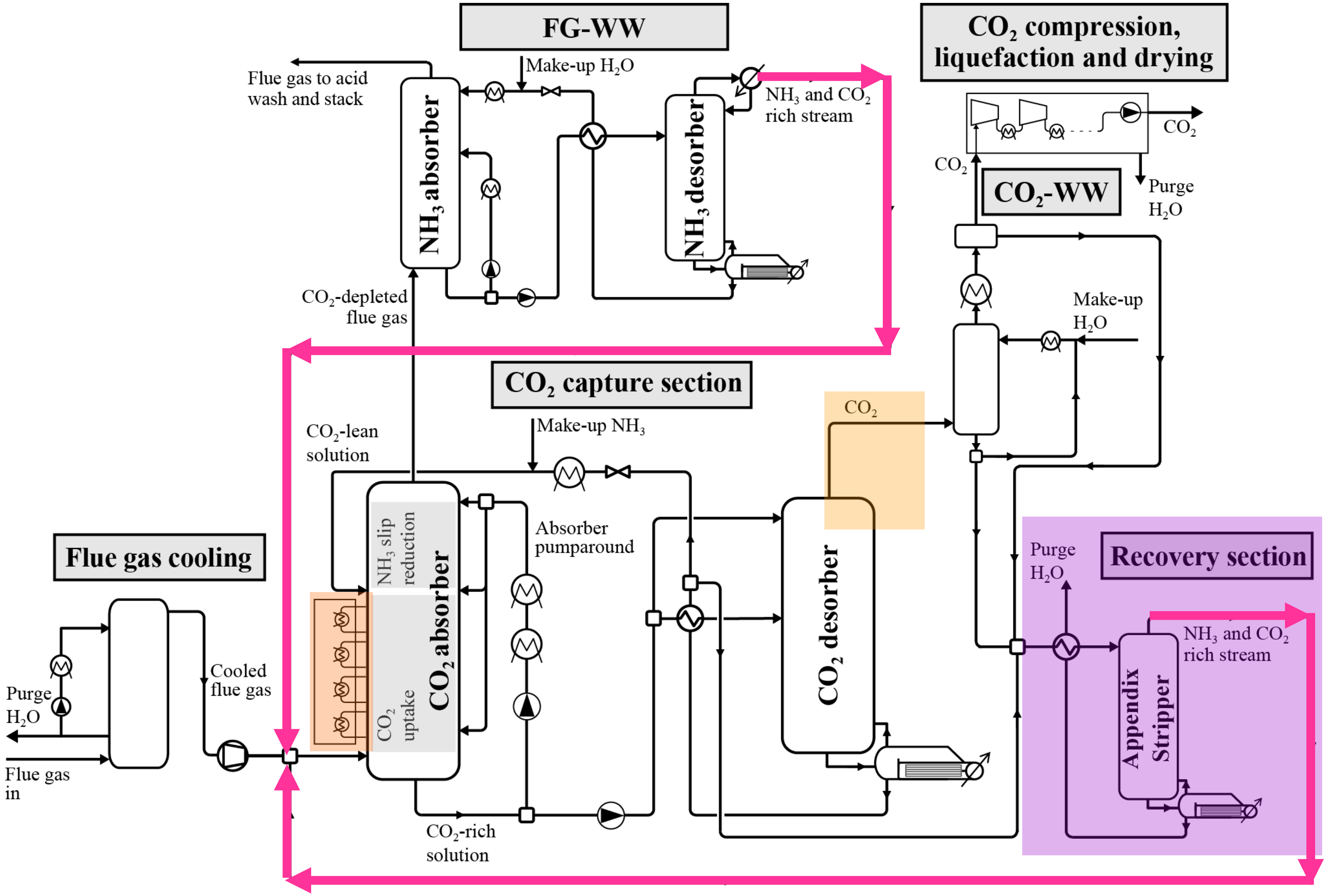
Process synthesis – Towards the CAP for cement application



General modifications/improvements

- Solvent recovery section
- Recycle of the NH_3 and CO_2 rich streams
- Condenser removal in CO_2 desorber

Process synthesis – Towards the CAP for cement application



General modifications/improvements

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- Intercooling of CO_2 absorber

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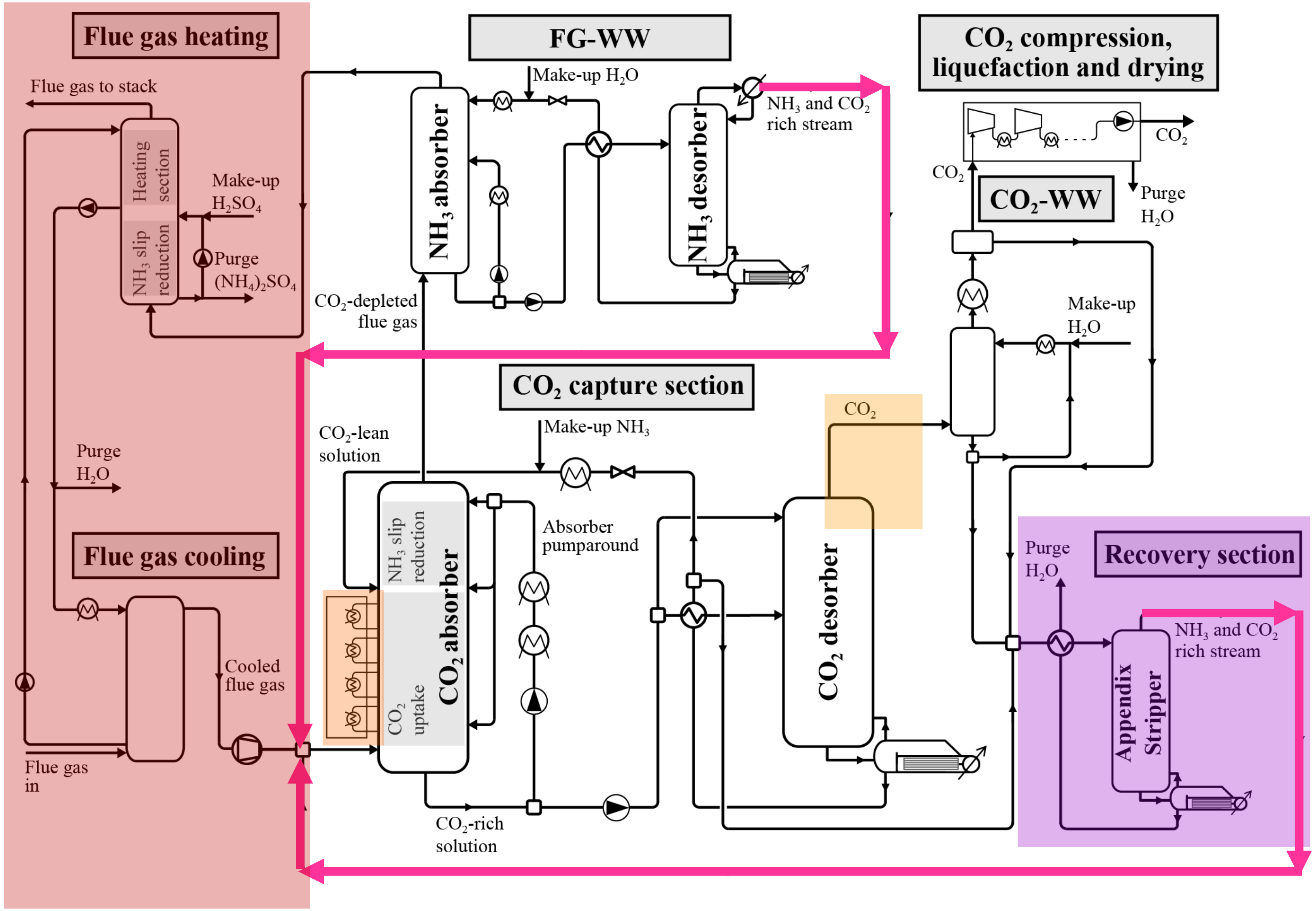

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- Solvent recovery section
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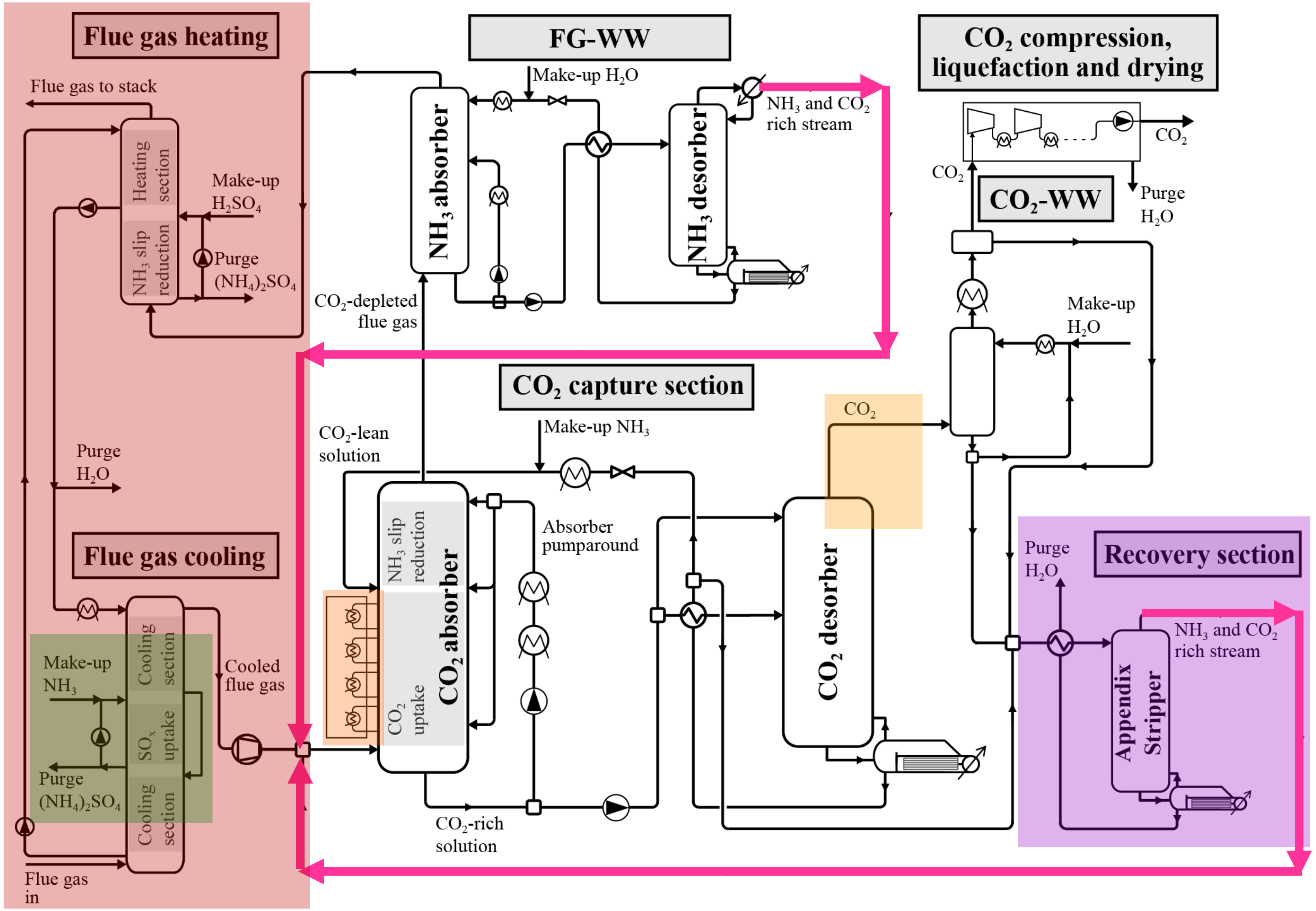
- Acid wash and DCC-DCH heat integration

Improvements specific to cement

Process synthesis – Towards the CAP for cement application



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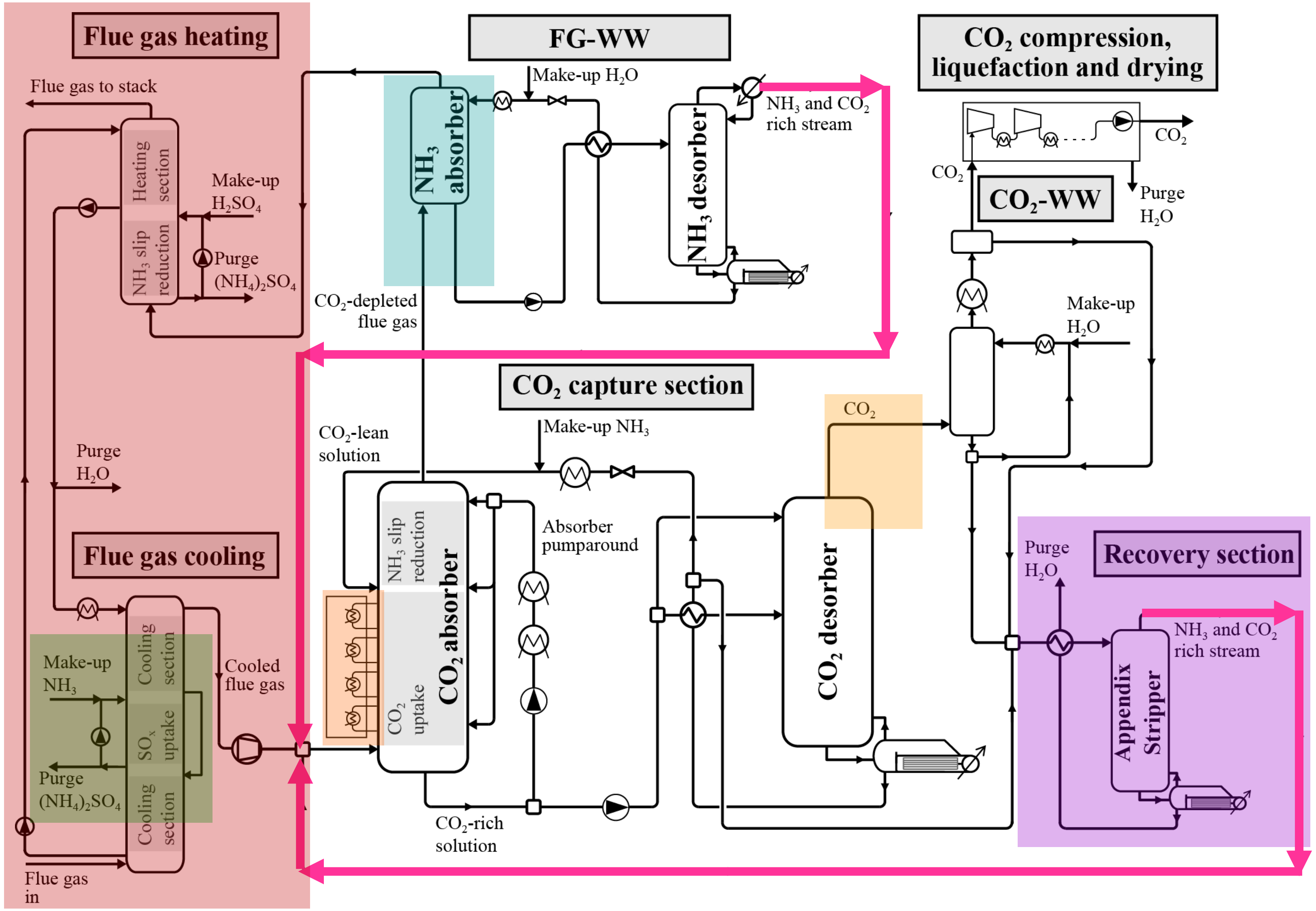
Improvements specific to cement

- $deSO_x$ by aqueous NH_3 solution

Process synthesis – Towards the CAP for cement application



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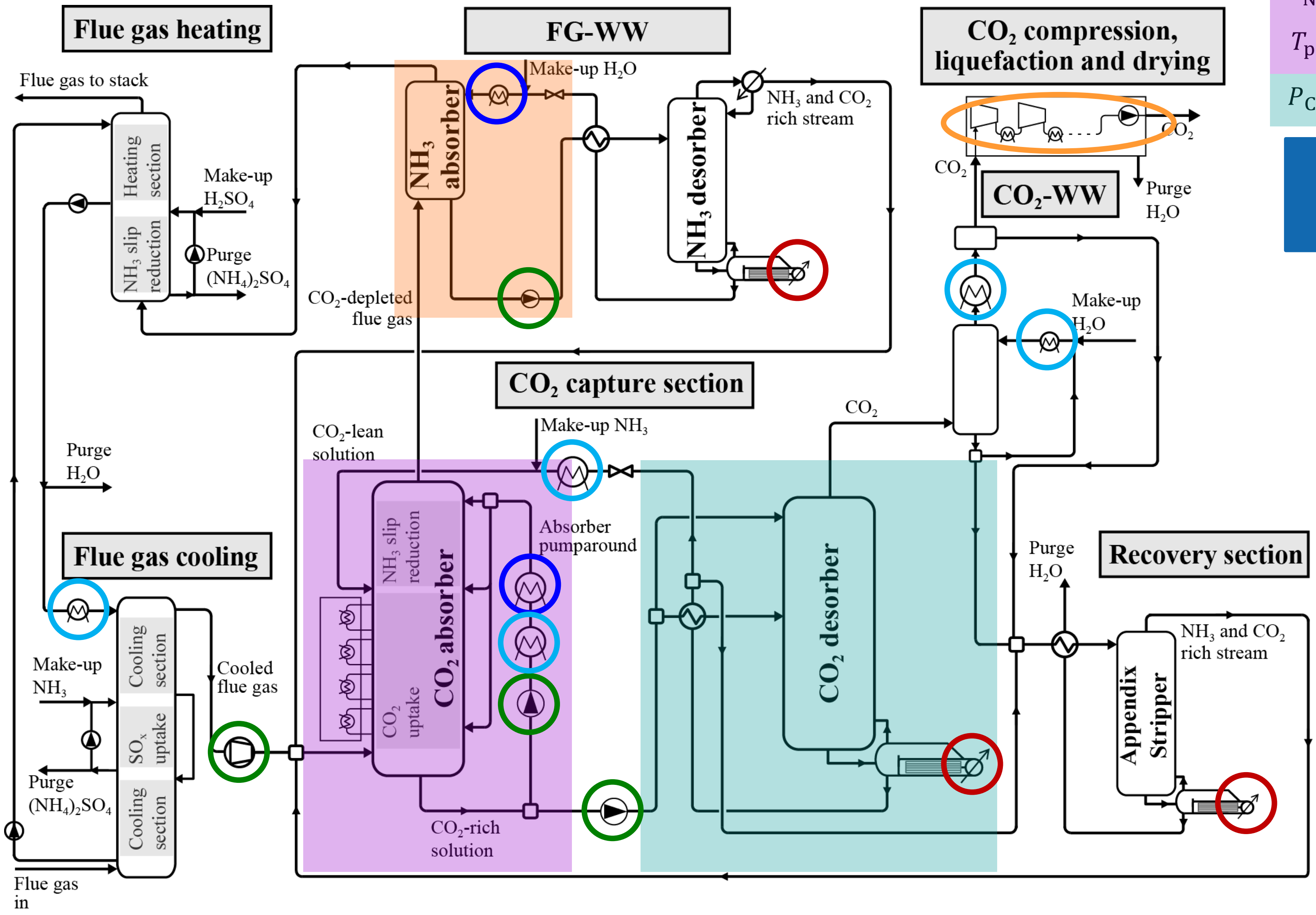
- Intercooling of CO_2 absorber
- Acid wash and DCC-DCH heat integration

Improvements specific to cement

- deSO_x by aqueous NH_3 solution
- Simplification of the NH_3 absorber

Heuristic process optimization



c_{NH_3}	$l_{CO_2}^{lean}$	L/G
T_{pa}	f_s	$c_{NH_3}^{FG-WW}$
$P_{CO_2 des}$	f_{cr}	$(L/G)^{FG-WW}$

SPECCA
(**S**pecific **P**rimary **E**nergy **C**onsumption for **C**O$_2$ **A**voided)

Decision variables → **Multi-variable sensitivity analysis[1,2]** → **Objective function**

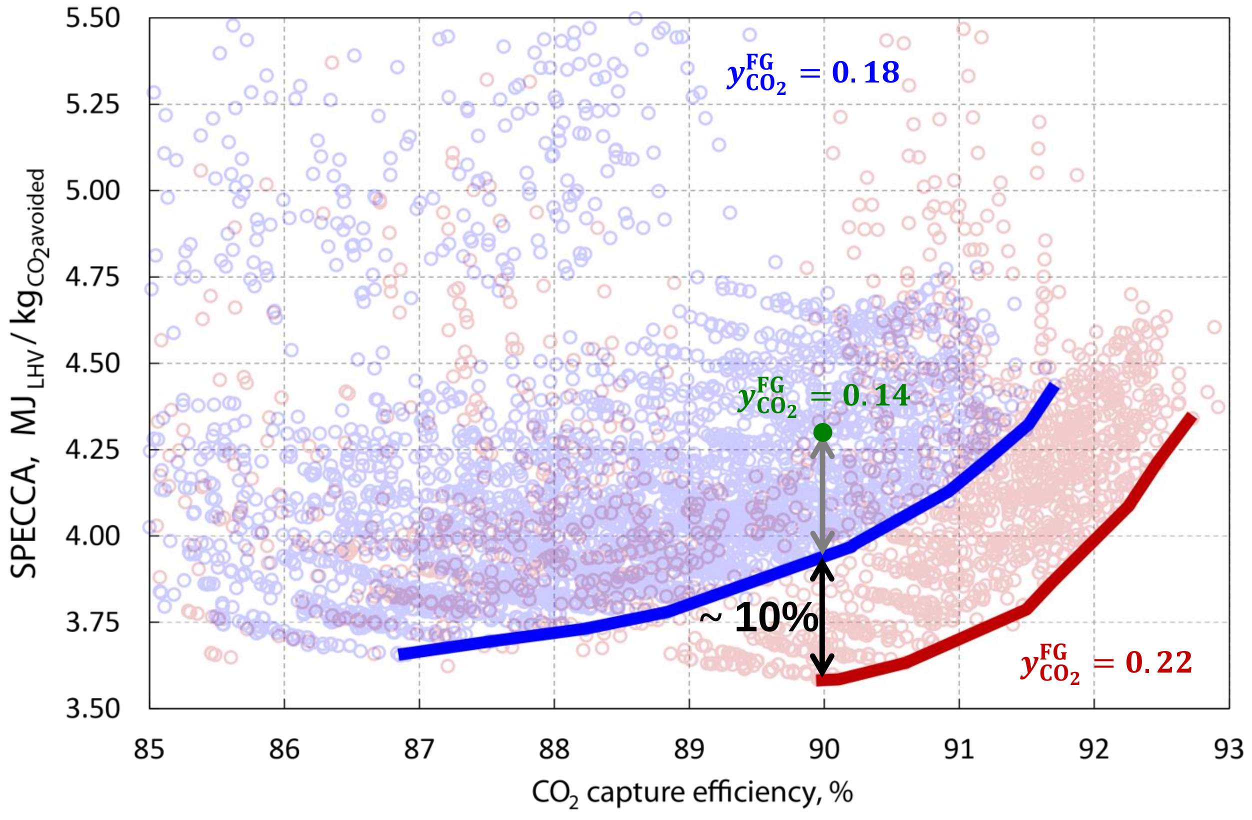
[1] Sutter et al. *Faraday Discuss* 192 (2016) 59-83
[2] Pérez-Calvo et al. *Energy Procedia* 114 (2017) 6197-205

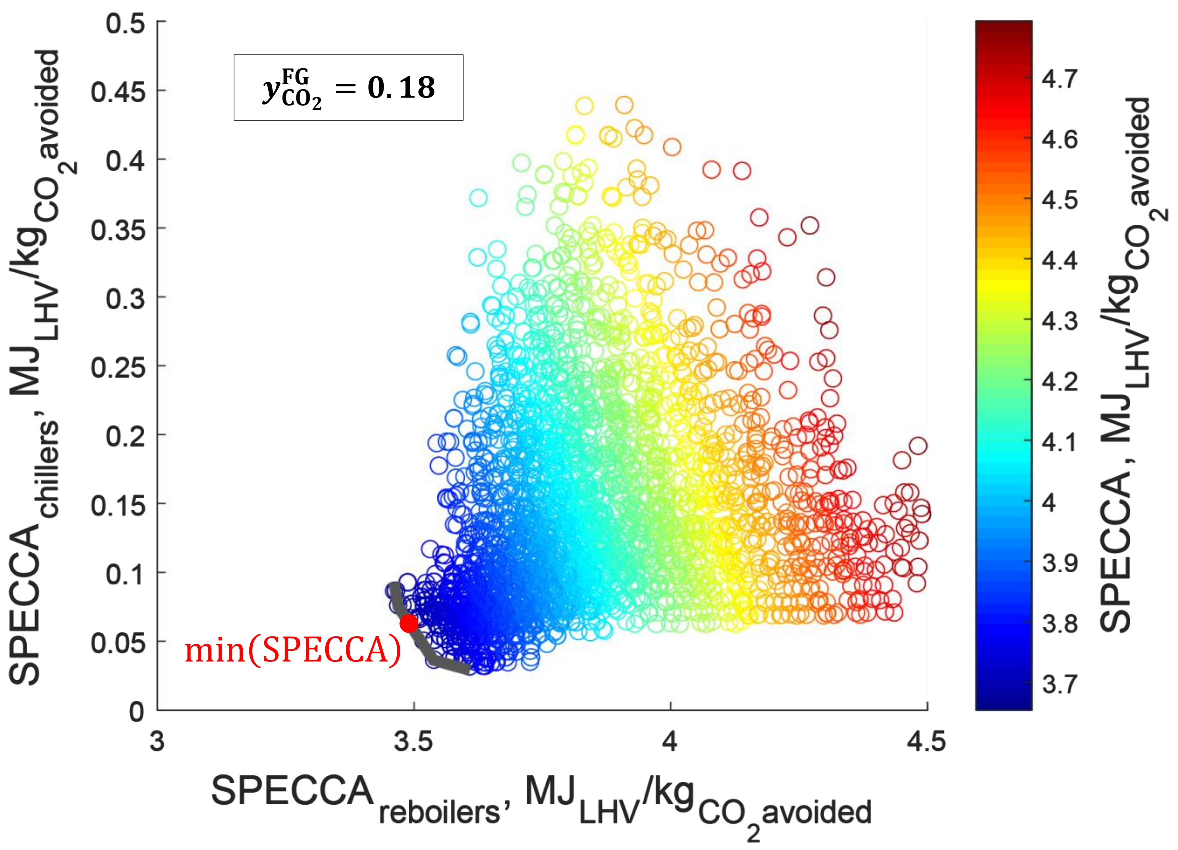
Specifications and constraints[3]

- 18 and 22%vol. CO_2
- CO_2 capture > 85 %
- NH_3 slip < 200 ppm (< 10 ppm at stack)
- CO_2 specifications for transport by pipeline
- No solid formation

[3] Voldsund et al. (2018) CEMCAP framework for comparative techno-economic analysis of CO_2 capture from cement plants (D3.2)

Process optimization – Results





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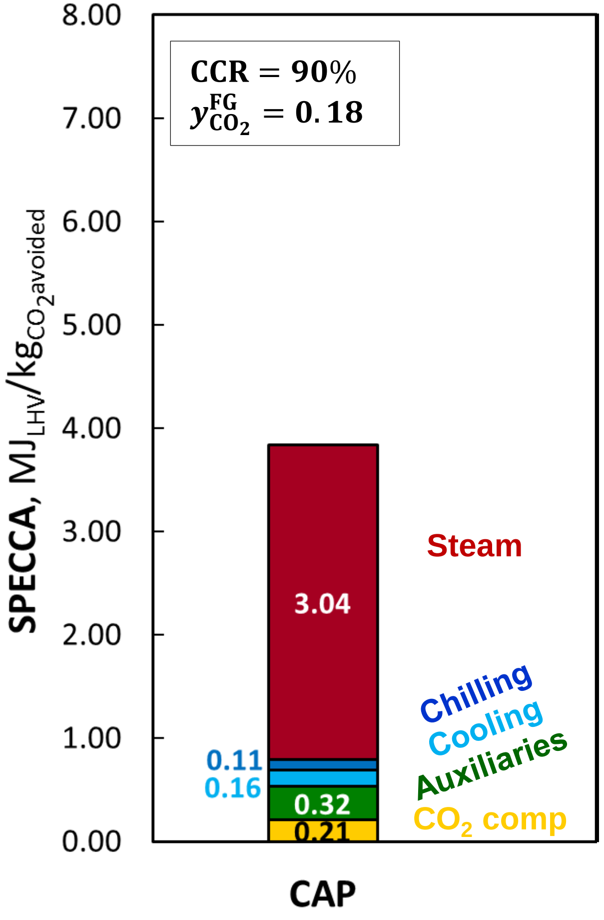
Overall energy performance



$C_{NH_3} = 6\ mol_{NH_3}/kg_{H_2O}$

$l_{CO_2}^{lean} = 0.39\ mol_{CO_2}/mol_{NH_3}$

$L/G = 6.5\ kg/kg$

$T_{pa} = 9\ °C$

$f_s = 0.18$

$P_{CO_2 des} = 25\ bar$

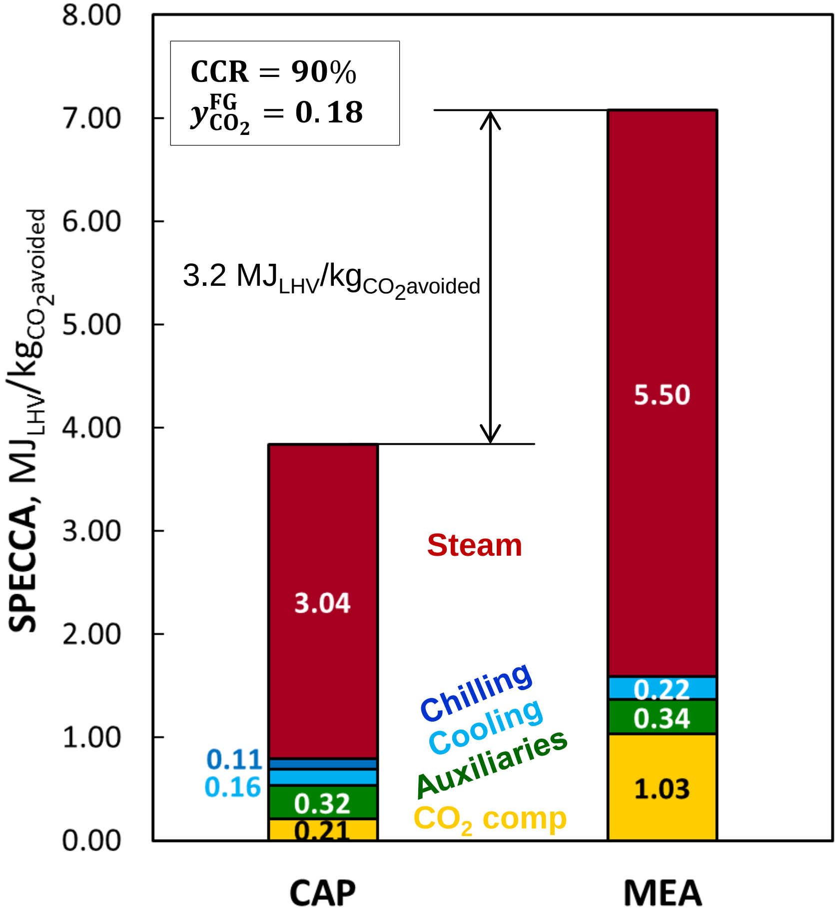
$f_{cr} = 0.035$

$C_{NH_3}^{FG-WW} = 0.05\ mol_{NH_3}/kg_{H_2O}$

$(L/G)^{FG-WW} = 0.2\ kg/kg$

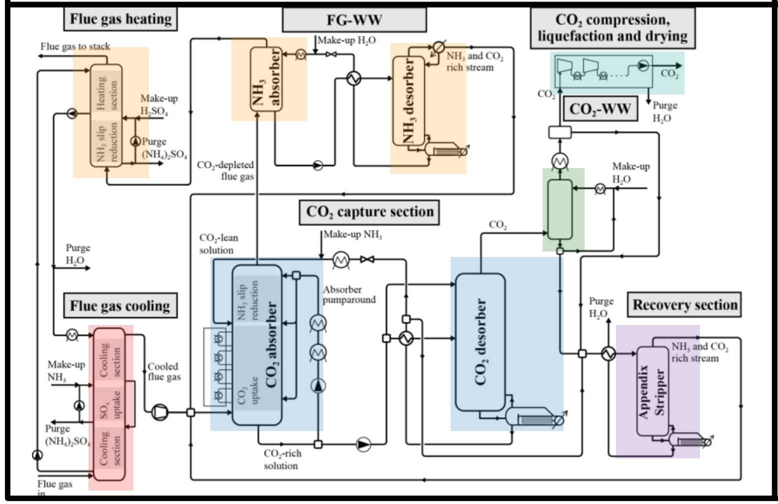
The CAP vs Amine-based capture processes for cement

L_{packing}	23.5	~ 10 – 30	[m]
$Q_{\mathrm{reb,CO_2}}$	2.1	~ 2.5 – 3.8	$\left[\frac{\mathrm{MJ_{th}}}{\mathrm{kg_{CO_2 captured}}}\right]$

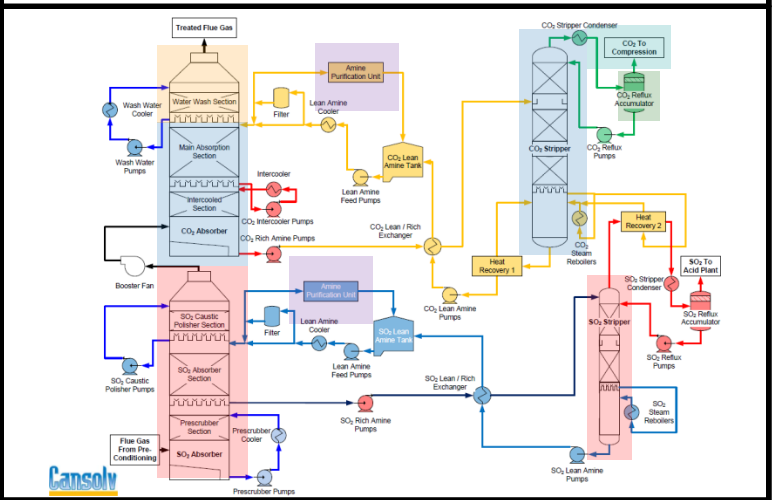


Anantharaman et al. (2017) Design and performance of CEMCAP cement plant with MEA post combustion capture (D4.2 CEMCAP)

Chilled Ammonia



Amines



- Similar process complexity
- NH_3 does not degrade
- CAP requires very low thermal energy for regeneration
- NH_3 is globally available
- NH_3 has lower environmental footprint and cost

- CO_2 absorption – desorption
- FG pre-conditioning (SO_x removal)
- FG post-conditioning
- Solvent recuperation/reclaiming
- CO_2 purification
- CO_2 compression

Conclusions

1) The CAP shows a very promising performance with respect to amine-based capture processes for cement application
   - Approx. 50% energy savings vs. MEA capture process
   - Similar height of the CO_2 absorber and number of unit operations
   - Vast experience, ready for large-scale demonstration for the cement plant application

2) The performance of the CAP applied to cement plants improves with respect to the power plant application
   - The high CO_2 concentrations can be exploited to minimize the energy consumption of the process with minor adaptations
   - The removal of residual NH_3 from the treated flue gas is favored by the high CO_2 concentration
   - The SO_2 removal can be integrated with the CAP by applying a diluted aqueous NH_3 solution

3) Improvements have been quantified and new process operating conditions have been obtained using a model-based optimization
   - Model developed on the grounds of 150 successful pilot plant tests performed at typical cement plant conditions: CO_2 absorber, de-SO_x unit and NH_3 absorber

4) New and advanced CAP configurations have been implemented

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement no 641185

This work was supported by the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract number 15.0160

The authors would like to thank Kaj Thomsen (Department of Chemical and Biochemical Engineering, Technical University of Denmark) for making the thermodynamic model available and for providing the relevant software

ETH zürich Utrecht University CEMCAP

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