

Modeling MEA Solvent Degradation in CO₂ Capture: A Comparison Applied to the Steel Manufacturing process

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Loris Baggio*
So-Mang Kim
Prof. Grégoire Léonard



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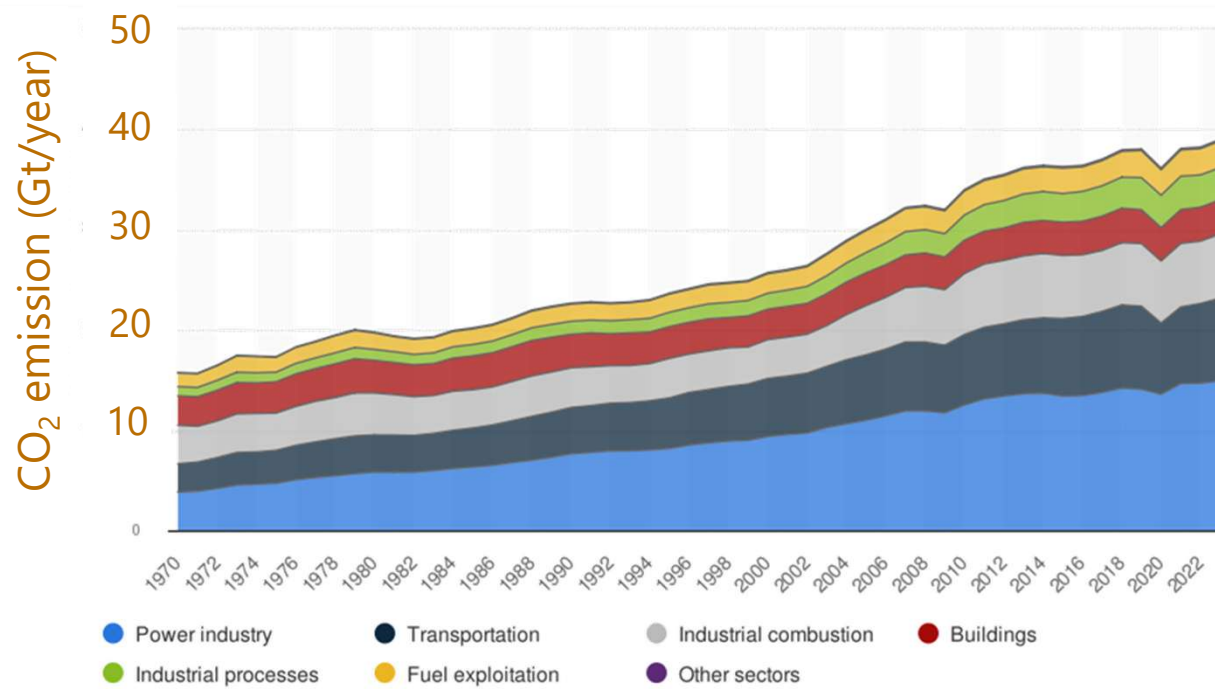
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Introduction

Global fossil CO₂ emissions from 1970 to 2023



Adapted from EDGAR/JRC; Expert(s) (Crippa et al (2024)); IEA; European Commission @Statista 2025



HECO2 – 5 – SATURN project

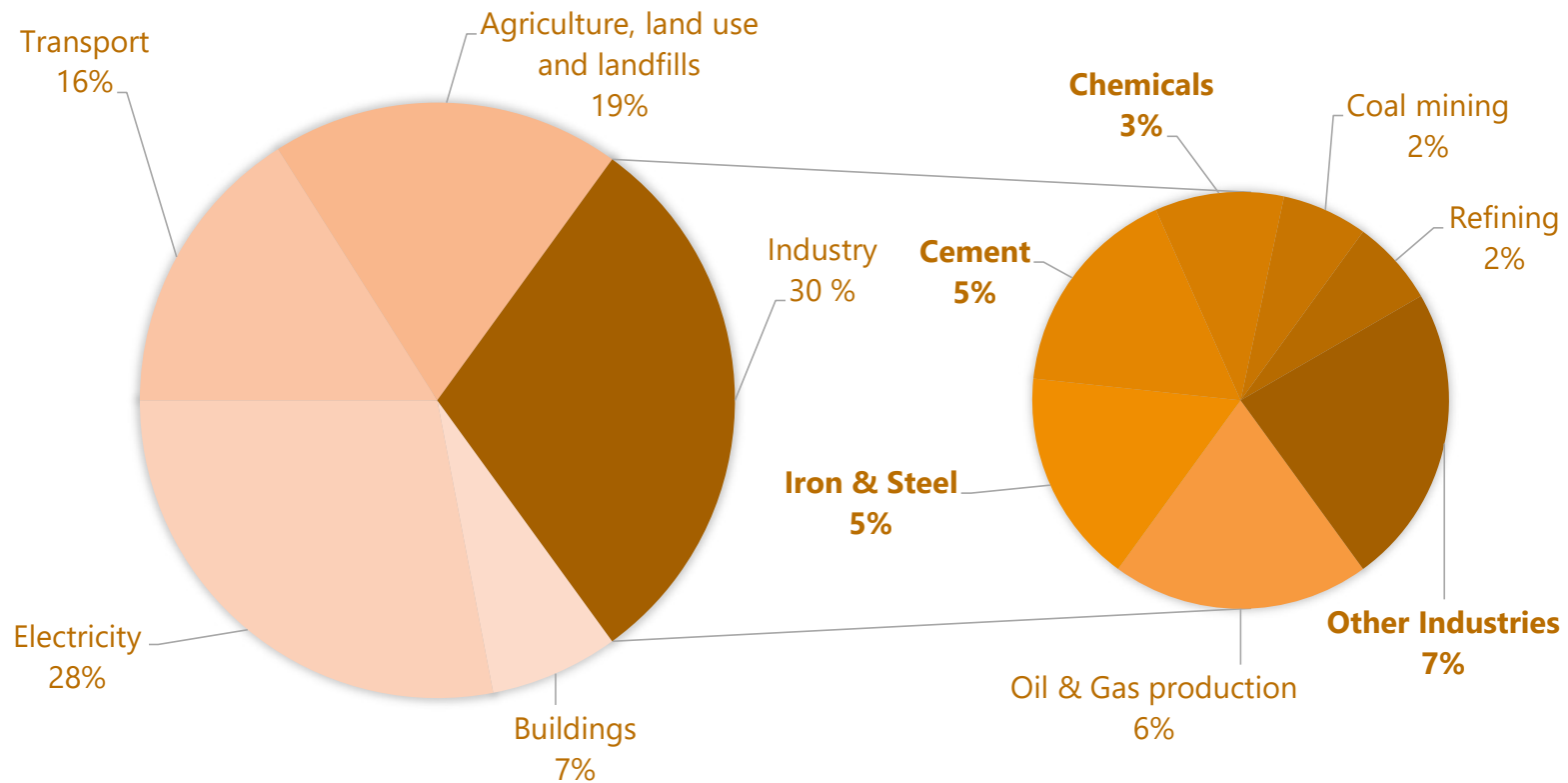


- ▶ Project financed by NextGenerationEU through Walloon region
- ▶ Part of 'HECO2: towards decarbonising Wallonia's heavy industry'
 - Axis 5: Carbon Capture Utilization & Storage (CCUS)
 - ▶ Bring together Universities, Research Centres & Industrial Partners
 - ▶ ULiège, UMONS, CRM, VOCSens, **AGC, APERAM, CARMEUSE, PRAYON**
 - ▶ **Glass, Steel, Lime & Chemicals sectors**
 - ▶ SATURN: Development and fine-tuning of a Post-Combustion CO₂ Capture process
 - ▶ Fixed and mobile Pilot Plant with two different technologies



Sectors involved

Global emissions by sector



Adapted from 'Global Greenhouse Gas Emissions: 1990-2022 and Preliminary 2023 Estimates'. Accessed: Jul. 04, 2025. [Online]. Available: <https://rhg.com/research/global-greenhouse-gas-emissions-1990-2022-and-preliminary-2023-estimates/>



CO₂ Capture Process by chemical absorption



▶ For '**hard-to-abate**' emissions → Post-Combustion capture is one of the solutions

○ Wide range of technologies

- ▶ Cryogenic & Membranes separation
- ▶ Physical & Chemical a**D**sorption
- ▶ Physical & Chemical a**B**sorption
- ▶ Combinations of them

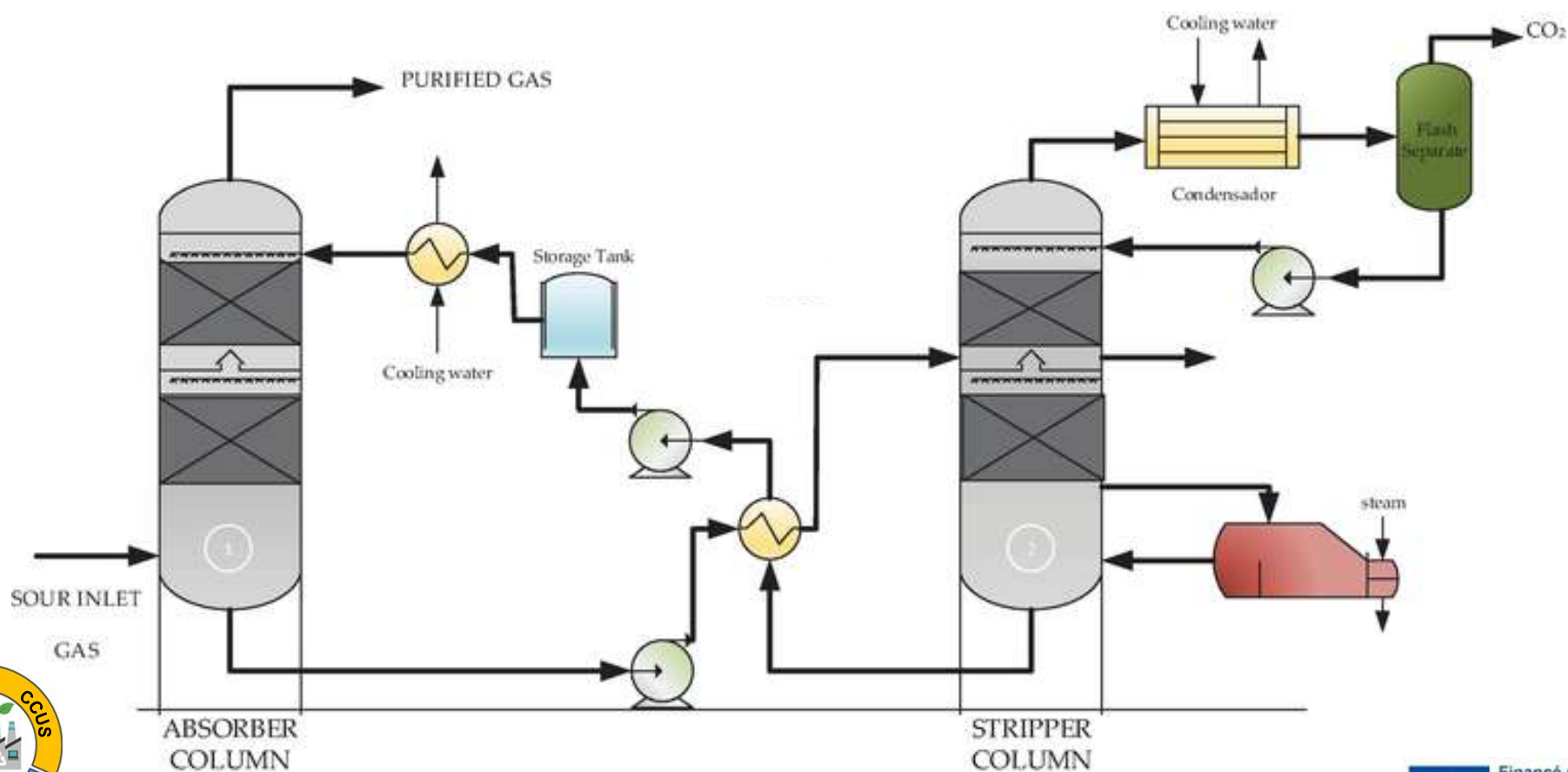
○ Most suitable technology → will depend on many KPIs (Key Performance Indicators)

- ▶ OPEX
- ▶ CAPEX
- ▶ Energy Consumption
- ▶ ...

○ However, CO₂ Capture by **Liquid Amine Absorption-Regeneration Process** is currently, the most widespread technology and is more mature (TRL 9)



Process Description



F. Vega, M. Cano, S. Camino, L. M. G. Fernández, E. Portillo, and B. Navarrete, 'Solvents for Carbon Dioxide Capture', in *Carbon Dioxide Chemistry, Capture and Oil Recovery*, I. Karamé, J. Shaya, and H. Srou, Eds., InTech, 2018. doi: [10.5772/intechopen.71443](https://doi.org/10.5772/intechopen.71443).

Process Description

- Chemical reactions involved with MEA in aqueous solvent

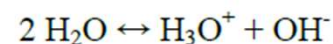
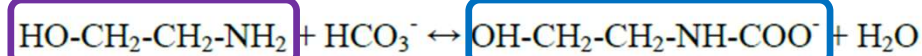
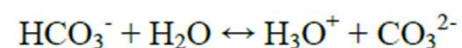
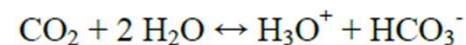
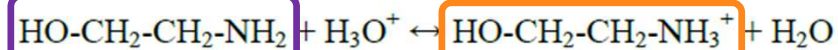
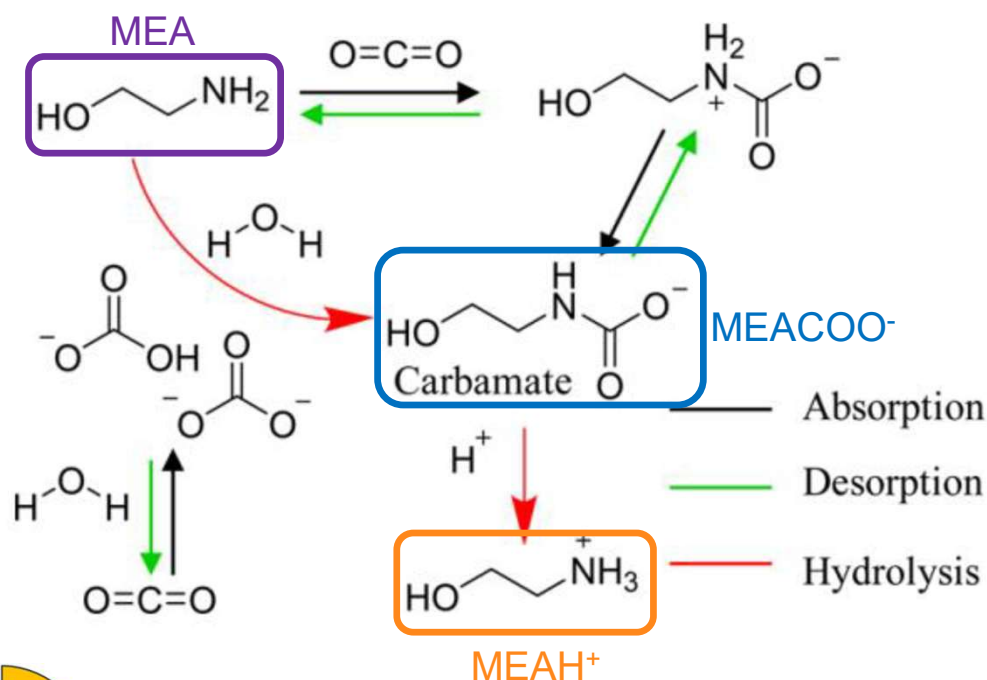


Figure adapted from **B. Lv, B. Guo, Z. Zhou, and G. Jing**, 'Mechanisms of CO₂ Capture into Monoethanolamine Solution with Different CO₂ Loading during the Absorption/Desorption Processes', *Environ. Sci. Technol.*, vol. 49, no. 17, pp. 10728–10735, Sep. 2015, doi: [10.1021/acs.est.5b02356](https://doi.org/10.1021/acs.est.5b02356).

Degradation Reactions

- ▶ But MEA could be degraded by different mechanisms
 - **Oxidative** degradation
 - **Thermal** degradation
 - Reactions of MEA with flue gas contaminants (**SO_x** & **NO_x**)
- ▶ Oxidative & Thermal degradation should also be included in the model
 - Oxidative degradation pathway based on Prof. Grégoire Léonard's work¹
 - ▶ $\text{MEA} + 1,3 \text{ O}_2 \rightarrow 0,6 \text{ NH}_3 + \text{HEI} + \text{HEPO} + \text{HCOOH} + 0,8 \text{ CO}_2 + 1,5 \text{ H}_2\text{O}$
 - Thermal degradation pathway based on Dr. Lucas' Braakhuis Thesis²
 - ▶ $2 \text{ MEA} \rightarrow \text{HEEDA} + \text{H}_2\text{O}$
 - ▶ $\text{MEA} + \text{HEEDA} \rightarrow \text{TRIMEA}$
 - ▶ $\text{HEEDA} + \text{CO}_2 \rightarrow \text{HEIA}$
 - ▶ $\text{TRIMEA} + \text{CO}_2 \rightarrow \text{AEHEIA}$
 - ▶ $2 \text{ MEA} \rightarrow \text{BHEU} + \text{H}_2\text{O}$



¹ G. Léonard, D. Toye, and G. Heyen, 'Experimental study and kinetic model of monoethanolamine oxidative and thermal degradation for post-combustion CO₂ capture', *International Journal of Greenhouse Gas Control*, vol. 30, pp. 171–178, Nov. 2014, doi: [10.1016/j.ijggc.2014.09.014](https://doi.org/10.1016/j.ijggc.2014.09.014).

² L. Braakhuis, 'Development of Solvent Degradation Models for Amine- Based CO₂ Capture', PhD Thesis, Norwegian University of Science and Technology, Trondheim, 2024. [Online]. Available: <https://ntnuopen.ntnu.no/ntnu-xmlui/handle/11250/3118629>

Process Modeling

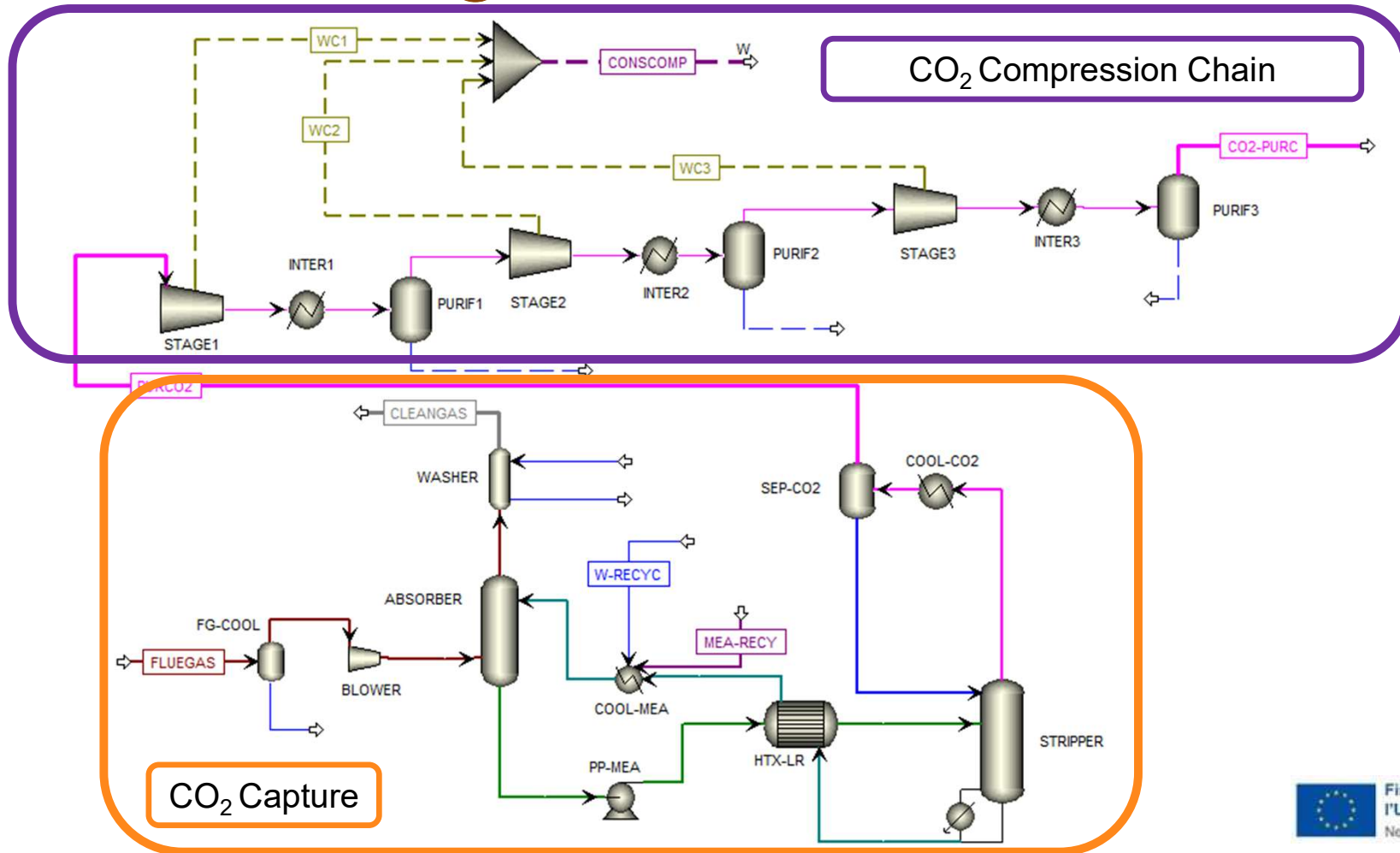


Modelling through ASPEN Plus software

- ▶ Rigorous simulation for columns
 - Rate-based model & Reaction kinetics
 - Accurate phase behavior and chemical speciation (CO₂-MEA-H₂O system)
- ▶ Thermodynamic models adapted to amine-based solvents
 - Electrolyte NRTL model for reactive systems
 - Properties estimation for special compounds
- ▶ Energy performance evaluation and process optimization
 - Sensitivity analysis on key variables (Reboiler Duty, O₂ Content, Amine Flowrate, etc.)
 - Optimization and Design specification (Capture rate)

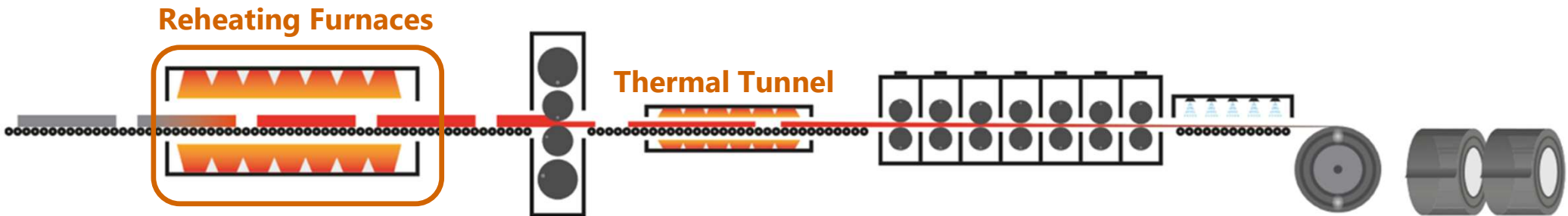


Process Modeling



Studied Case

- ▶ Hot Rolled Stainless Steel manufacturing
 - Exhaust gas from Reheating furnaces

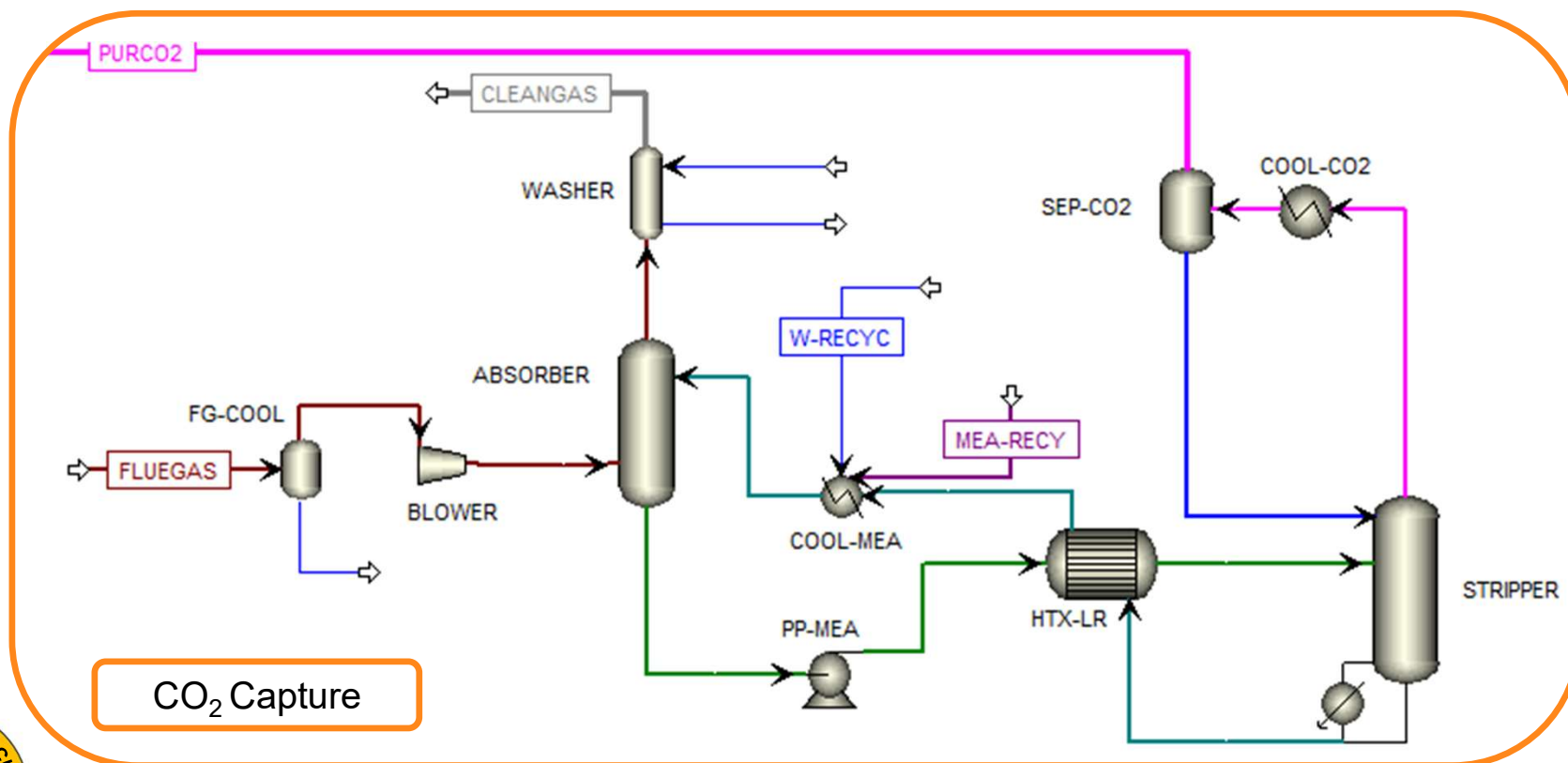


Parameters	Units	Value
Flowrate	[Nm ³ /h]	150 000
Temperature	[°C]	260
Pressure	[atm]	1

H ₂ O concentration	Vol.-%	15
CO ₂ concentration	Vol.-%	8
O ₂ concentration	Vol.-%	4
N ₂ concentration	Vol.-%	73



Studied Case



CO₂ Capture



Results

- ▶ Two main KPIs identified
 - Energy Consumption
 - MEA Loss
- ▶ Case 1 (without degradation) – Case 2 (Including Oxidative & Thermal Degradation)

Parameters	Unit	Case 1	Case 2
Energy consumption	(GJ/t CO ₂)	3.86	3.88
Captured CO₂	(t/h)	21.2	21.2
MEA solvent flowrate	(m ³ /h)	436	436
MEA concentration	(wt.-%)	30.04	30.03
MEA loss	(kg/t CO ₂)	10⁻⁴	0.189

*Not zero due to the combined effects of evaporation and degradation



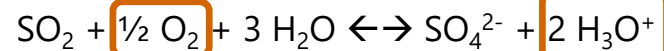
Next steps

▶ Reactions of MEA with flue gas contaminants (SO_x)

○ Initial modelling using **chemical equilibrium assumptions**

▶ 2 main reactions

▶ SO_4^{2-} formation :



▶ Heat Stable Salt formation :



Less O_2 available for oxidative degradation

2 MEA unusable

Acidification

○ Second approach with **kinetics and experimental results**

▶ Experimental setup

▶ $\text{CO}_2 - \text{O}_2 - \text{N}_2 - \text{SO}_2$ mixture

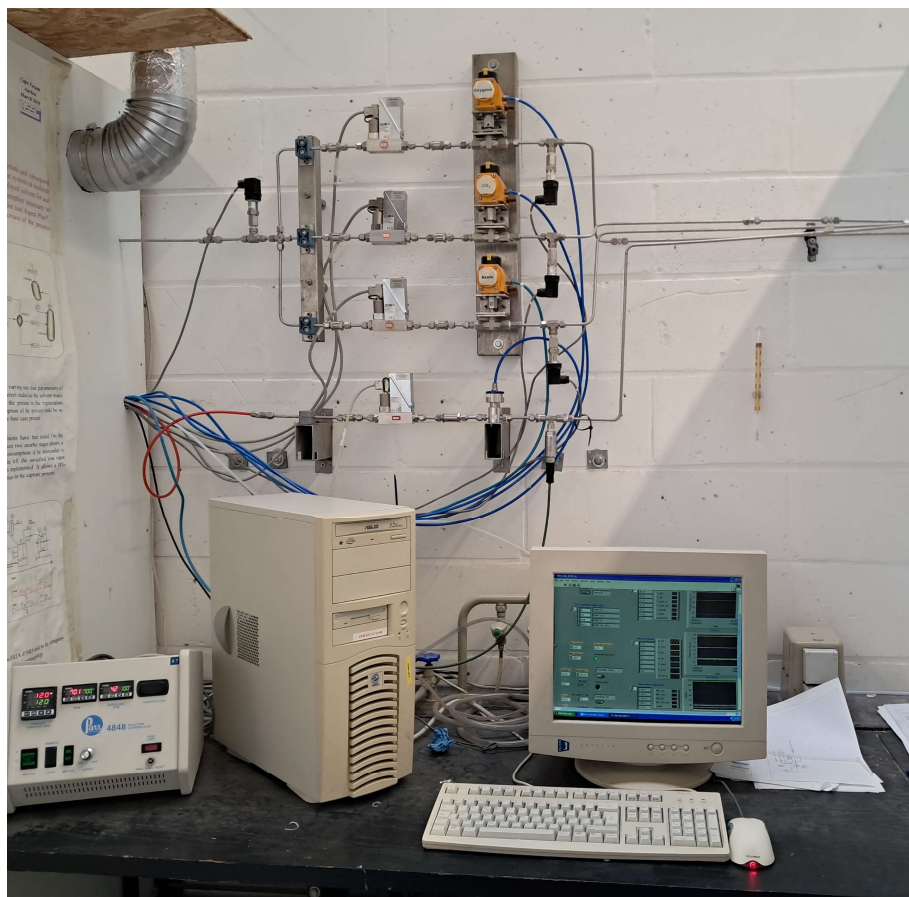
▶ Accelerated conditions (4 barg – 120 °C – 700 rpm)

▶ Analytical measurement

▶ Development of a kinetic model



Experimental setup (Degradation Test Rig)



Conclusion & Perspectives



- ▶ Even with a mature technology, there are still some challenges
 - Degradation has an impact on main KPIs
 - ▶ Environmental, Energetical & Economical
 - Modeling tends to be consistent with plant data
 - ▶ **0.189 kg MEA/t CO₂** in the range of **0.1 to 0.8 kg/t³**
 - It is one step towards derisking the technology for desired investment by Industries
 - ▶ More knowledge on the process → Less restraint to install this
- ▶ Continue refining it to improve precision and representativeness
- ▶ Extend the model to **new solvents** (CESAR1, ...) and to **the other sectors**



³**Neerup R et al.** Solvent degradation and emissions from a CO₂ capture pilot at a waste-to-energy plant. J Environ Chem Eng 11:111411 (2023) <https://doi.org/10.1016/j.jece.2023.111411>

Thank you for your attention!

Loris Baggio
So-Mang Kim
Grégoire Léonard

Contact: Loris Baggio
Email: loris.baggio@uliege.be

Key Sensitivity Parameters for CO₂ Capture



▶ What should be studied?

○ Variation of the **stripper pressure**

- ▶ ↑ Stripper desorption = ↓ Specific energy consumption
- ▶ But ↑ temperature achieved



○ Variation on **lean amine flowrate**

- ▶ Less flowrate = ↓ amine
- ▶ But ↑ specific energy consumption for the same capture rate



○ **Dynamic studies**

- ▶ Equilibrium vs Rate-Based model for columns
- ▶ Dynamic but with equilibrium columns...
- ▶ Loss of precision with small amounts, especially in our case



Degradation products

