SO_2 Influence on MEA Degradation in CO_2 Capture Absorption-Regeneration Process: Competition with Oxidative Degradation

World Trade Centre – Marseille, 17th of September 2025

Post-Combustion Capture Conference 8th , IEAGHG

Loris Baggio*
Prof. Grégoire Léonard

Financé par l'Union européenne
NextGenerationEU

Contents

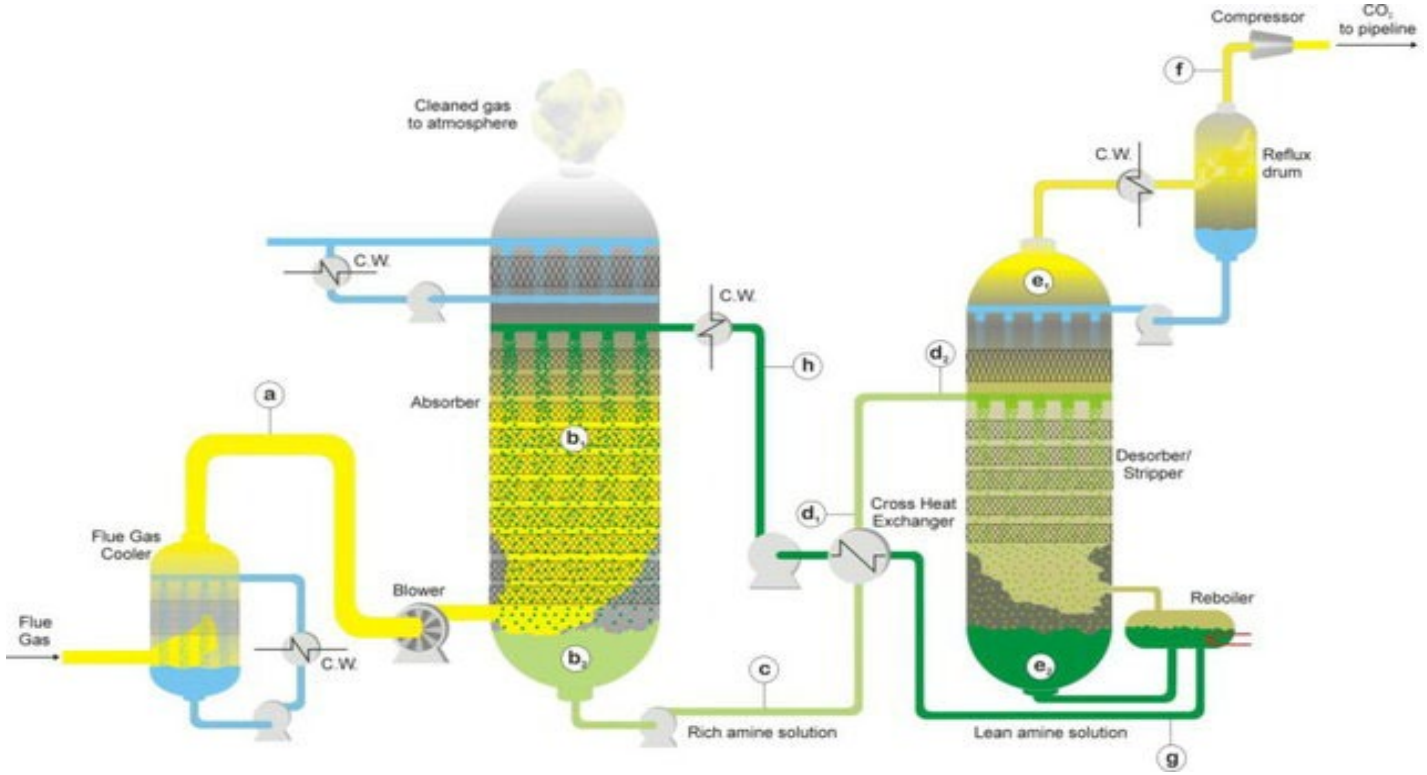
Financé par l'Union européenne NextGenerationEU

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
    - Post-combustion CO_2 capture process: development and optimization
      - Two different technologies are studied with two pilots
        - Cryogenic & **Chemical Absorption-Regeneration**

Introduction

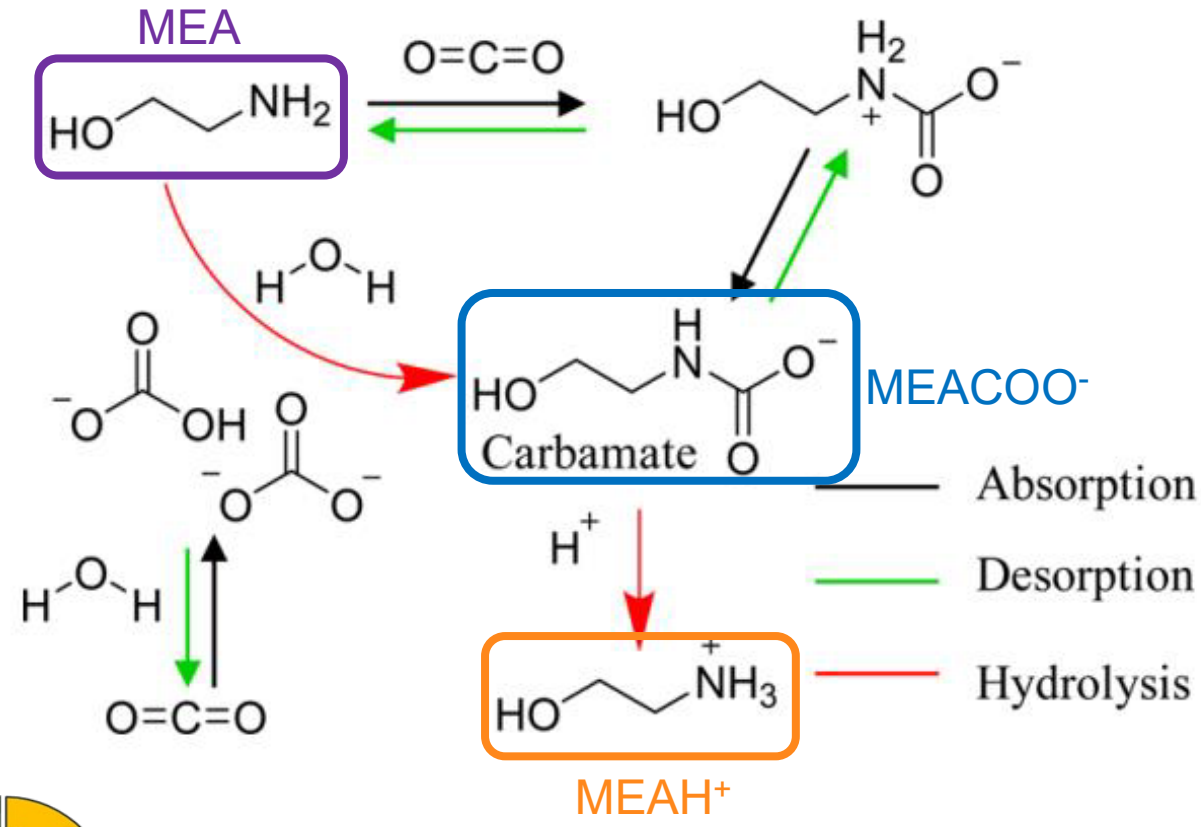
- For '**hard-to-abate**' emissions → Post-Combustion capture is one of the solutions
  - Wide range of technologies (cryogenic, membrane, adsorption, absorption,…)
    - **Liquid amine absorption–regeneration process = widespread and more mature (TRL ++)**



A. Krzemień, A. Więckol-Ryk, A. Duda, and A. Koteras, 'Risk Assessment of a Post-Combustion and Amine-Based CO2 Capture Ready Process', *Journal of Sustainable Mining*, vol. 12, no. 4, pp. 18–23, 2013, doi: 10.7424/jsm130404.

Process Description

- Chemical reactions involved with MEA in aqueous solvent



MEA

$HO\text{-}CH_2\text{-}CH_2\text{-}NH_2 + H_3O^+ \leftrightarrow$ MEAH+ $HO\text{-}CH_2\text{-}CH_2\text{-}NH_3^+ + H_2O$

$CO_2 + 2\,H_2O \leftrightarrow H_3O^+ + HCO_3^-$

$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$

MEACOO- $HO\text{-}CH_2\text{-}CH_2\text{-}NH_2 + HCO_3^- \leftrightarrow OH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}COO^- + H_2O$

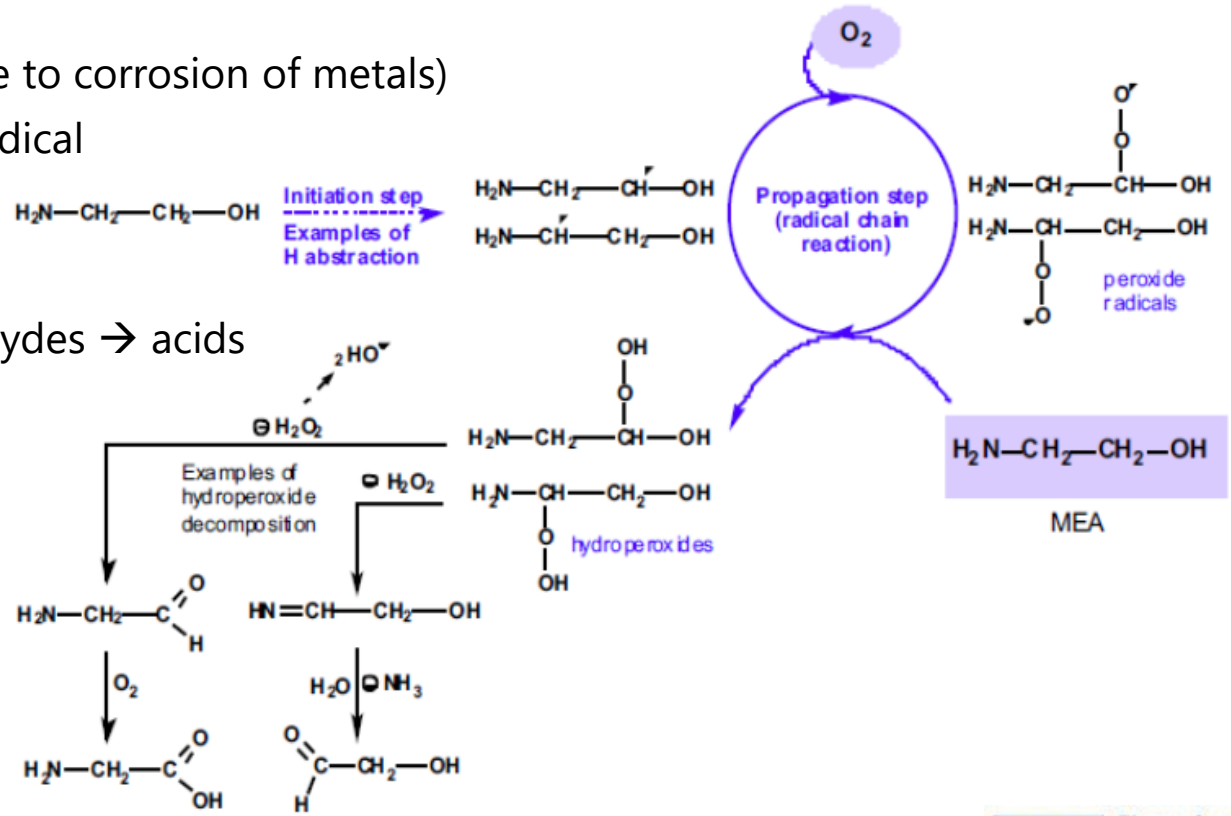
$2\,H_2O \leftrightarrow H_3O^+ + OH^-$

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.

Financé par l'Union européenne NextGenerationEU

Degradation of Amine Solvent

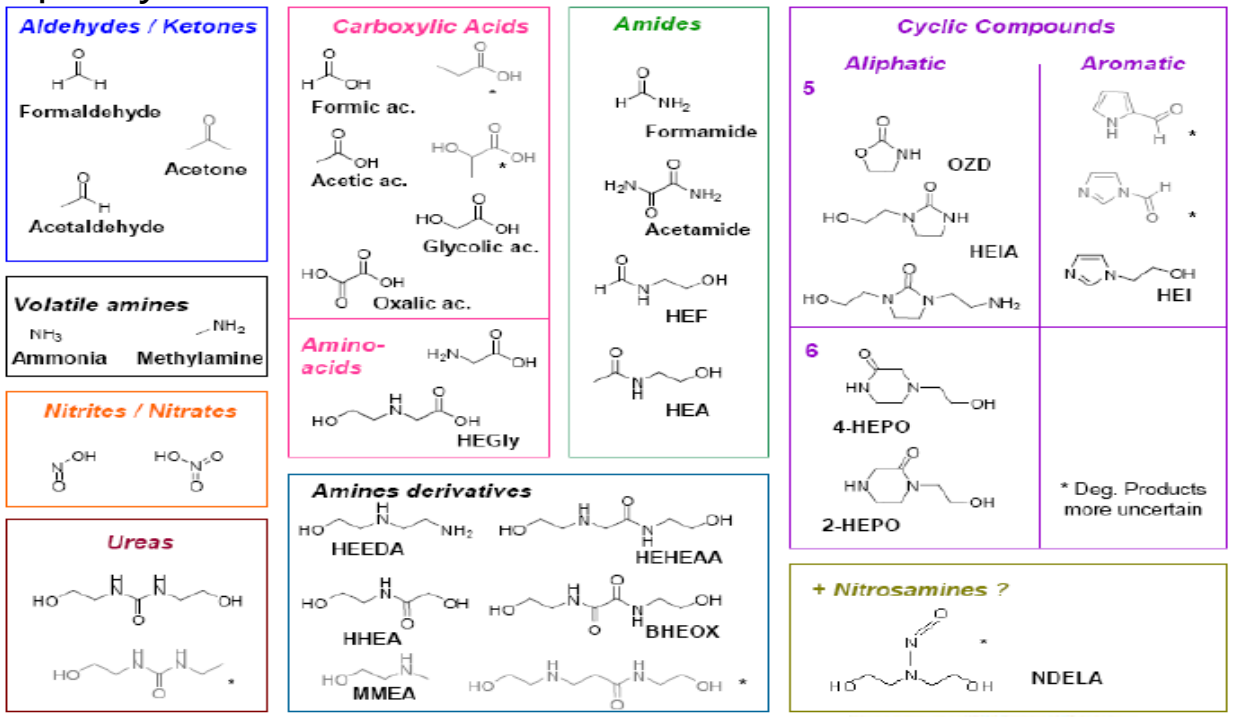
- But MEA could be degraded by different mechanisms
  - **Oxidative** degradation
    - Initiation
      - O_2 drive radical formation
      - Fe/Cu/Mn catalyze reactions (due to corrosion of metals)
      - ·OH / ·OOH abstract H → MEA radical
    - Propagation
      - MEA radicals + O_2 → peroxides
      - $-CH_2OH/-NH_2$ oxidation → aldehydes → acids

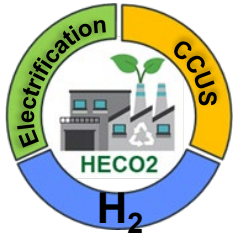


B. Delfort, P.-L. Carrette, and L. Bonnard, 'MEA 40% with improved oxidative stability for CO2 capture in post-combustion', *Energy Procedia*, vol. 4, pp. 9–14, 2011, doi: 10.1016/j.egypro.2011.01.016.

Degradation of Amine Solvent

- Products & Operational Consequences
  - **H**eat **S**table **S**alts (Formate, Acetate, Oxalate, Glycolate, …)
    - Solvent loss, higher reclaiming, reduced CO_2 capacity, corrosion
  - Ammonia, Aldehyde, Organic Amides
    - Volatile, emission concerns
  - Cyclic Compounds & Amine derivatives
    - Increase viscosity, foaming, process handling





G. Léonard, 'Optimal design of a CO_2 capture unit with assessment of solvent degradation', PhD Thesis, Université de Liège, Liège, 2013. Accessed: Sept. 12, 2023. [Online]. Available: https://orbi.uliege.be/handle/2268/152320

Financé par l'Union européenne NextGenerationEU

Degradation of Amine Solvent

- Reactions of MEA with flue gas contaminants (SO_x)
  - 2 main reactions are identified
    - SO_4^{2-} formation (condensed version) : SO_2 + ½ O_2 + 3 H_2O → SO_4^{2-} + 2 H_3O^+
      - ½ O_2: Less O_2 available for oxidative degradation
      - 2 H_3O^+: Acidification
    - Heat Stable Salt formation : SO_4^{2-} + 2 MEA^+ → HSS
      - 2 MEA^+: 2 MEA unusable but not degraded in amine derivative

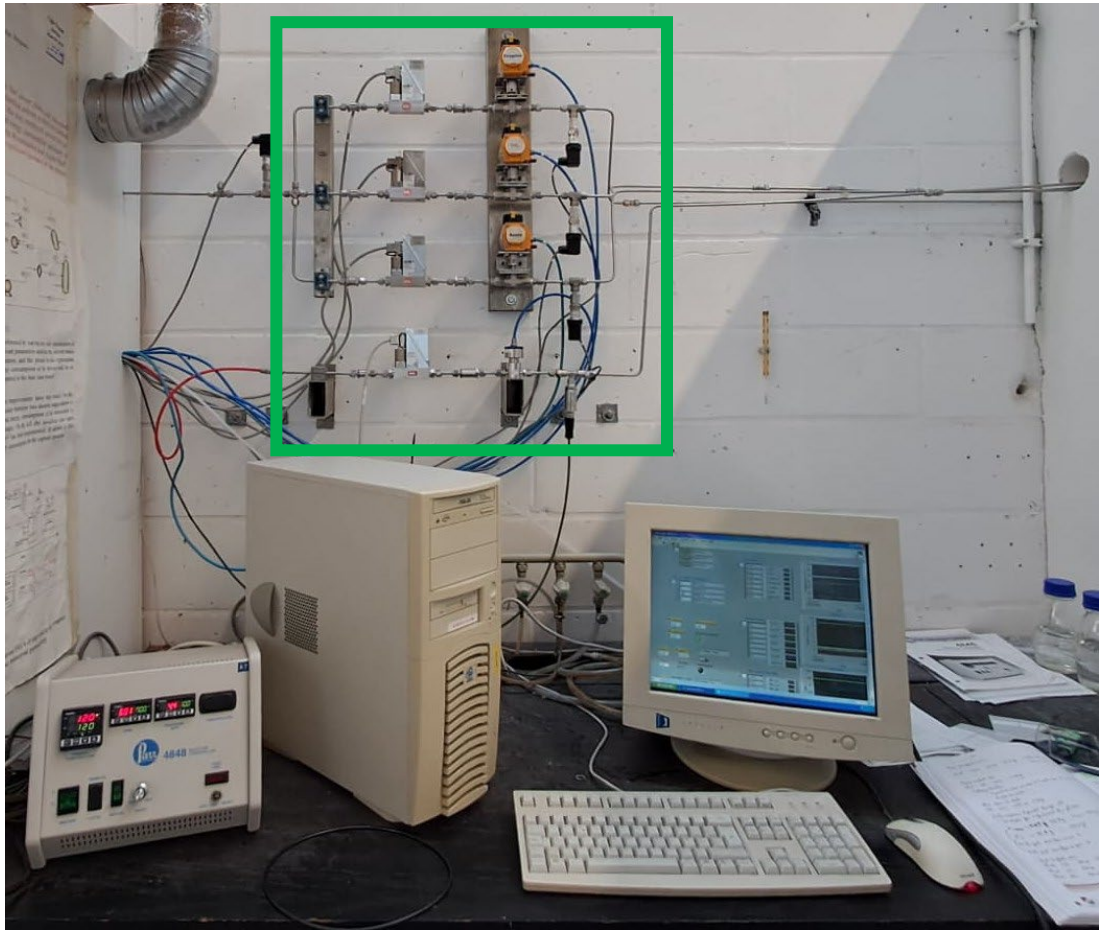
Degradation Test Rig

- **Degradation Tests in presence of SO_2**
  - MEA 30 wt.-% solvent prepared in lab and loaded with CO_2 until ~0.5 mol CO_2/mol MEA
    - Accelerated degradation conditions (120°C, 4 barg, agitation speed of 700 rpm)
    - Semi-batch system (inlet/outlet gas & solvent in the reactor)
      - **Stainless-Steel** Reactor
      - **PTFE** liner available
  - Base case validated during PhD Thesis of Prof. G. Léonard[1]
    - Ternary mixture O_2 – CO_2 – N_2 with **15% CO_2 – 5% O_2**

[1]G. Léonard, 'Optimal design of a CO2 capture unit with assessment of solvent degradation', PhD Thesis, Université de Liège, Liège, 2013. Accessed: Sept. 12, 2023. [Online]. Available: https://orbi.uliege.be/handle/2268/152320

Financé par l'Union européenne NextGenerationEU

Degradation Test Rig

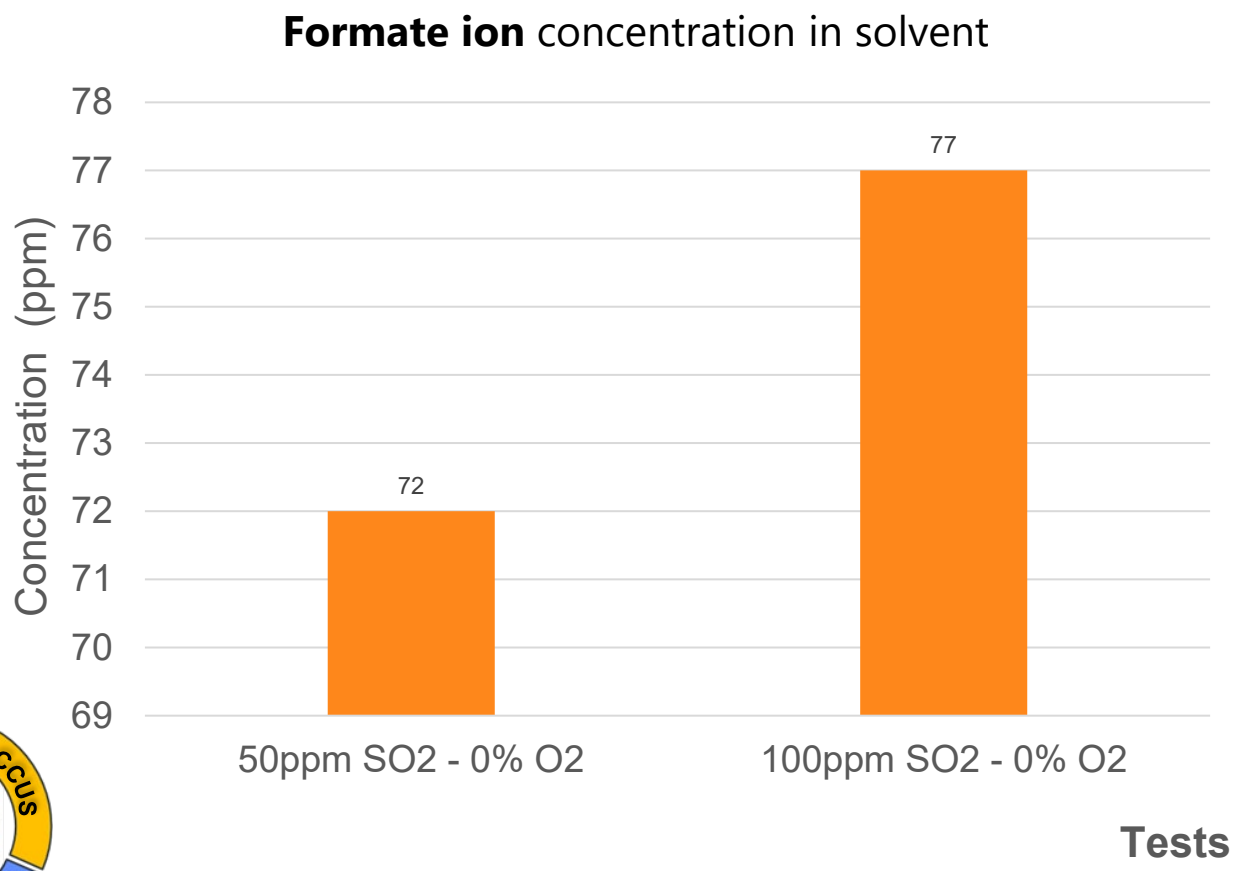


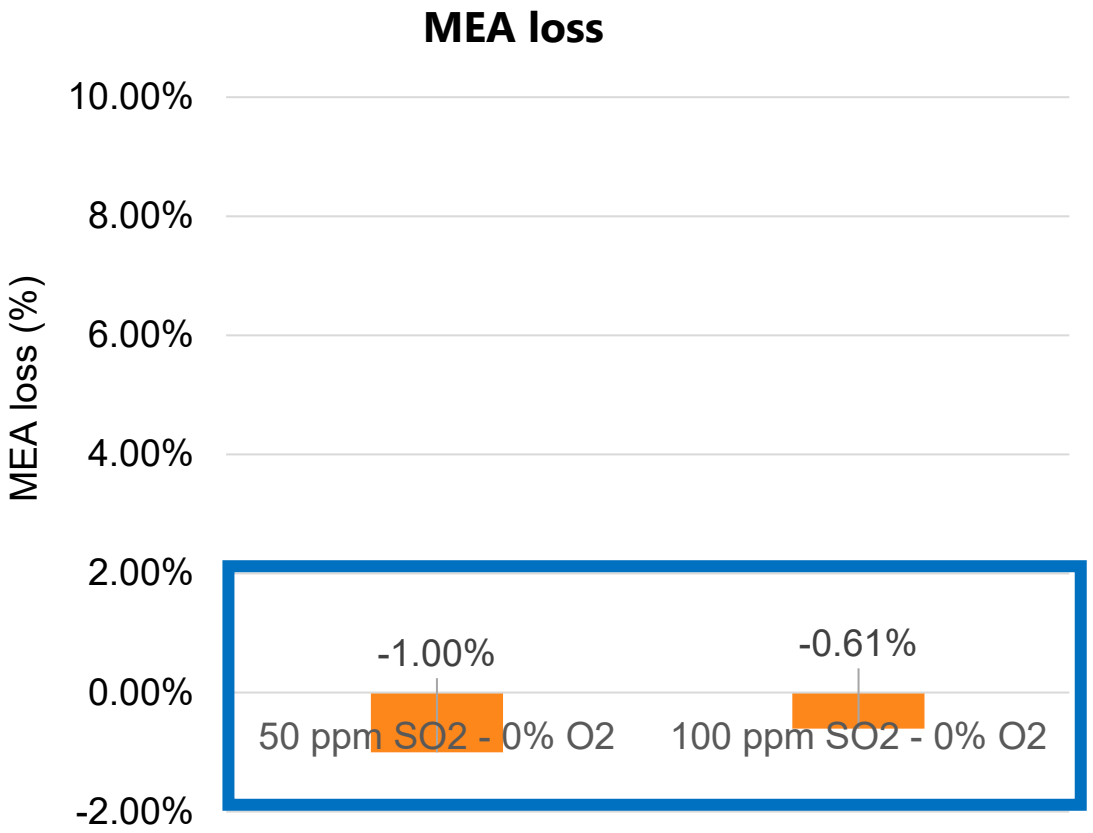
Degradation Test Rig

- Tests with quaternary mixture SO_2 – N_2 – O_2 – CO_2
  - 4 kinds of tests with 3 approaches (for now)
    - 50 and 100 ppm SO_2 in the **Stainless-Steel** reactor **without O_2**
      - Check the non MEA degradation
    - 50 and 100 ppm SO_2 in the **Stainless-Steel** reactor **with 5% O_2**
      - Corrosion and influence of SO_2 on oxidative degradation
    - 50 and 100 ppm SO_2 in the **PTFE** reactor **with 5% O_2**
      - Isolation of SO_2 reactions & oxidative degradation competition
    - 100 ppm SO_2 in the **PTFE** reactor **with 2,5 and 10% O_2**
      - Impacts of O_2 in the presence of SO_2

Results

- IC² & HPLC analysis for the **Stainless-Steel** reactor without O_2
  - 0 % O_2 – 15 % CO_2 – 50/100 ppm SO2

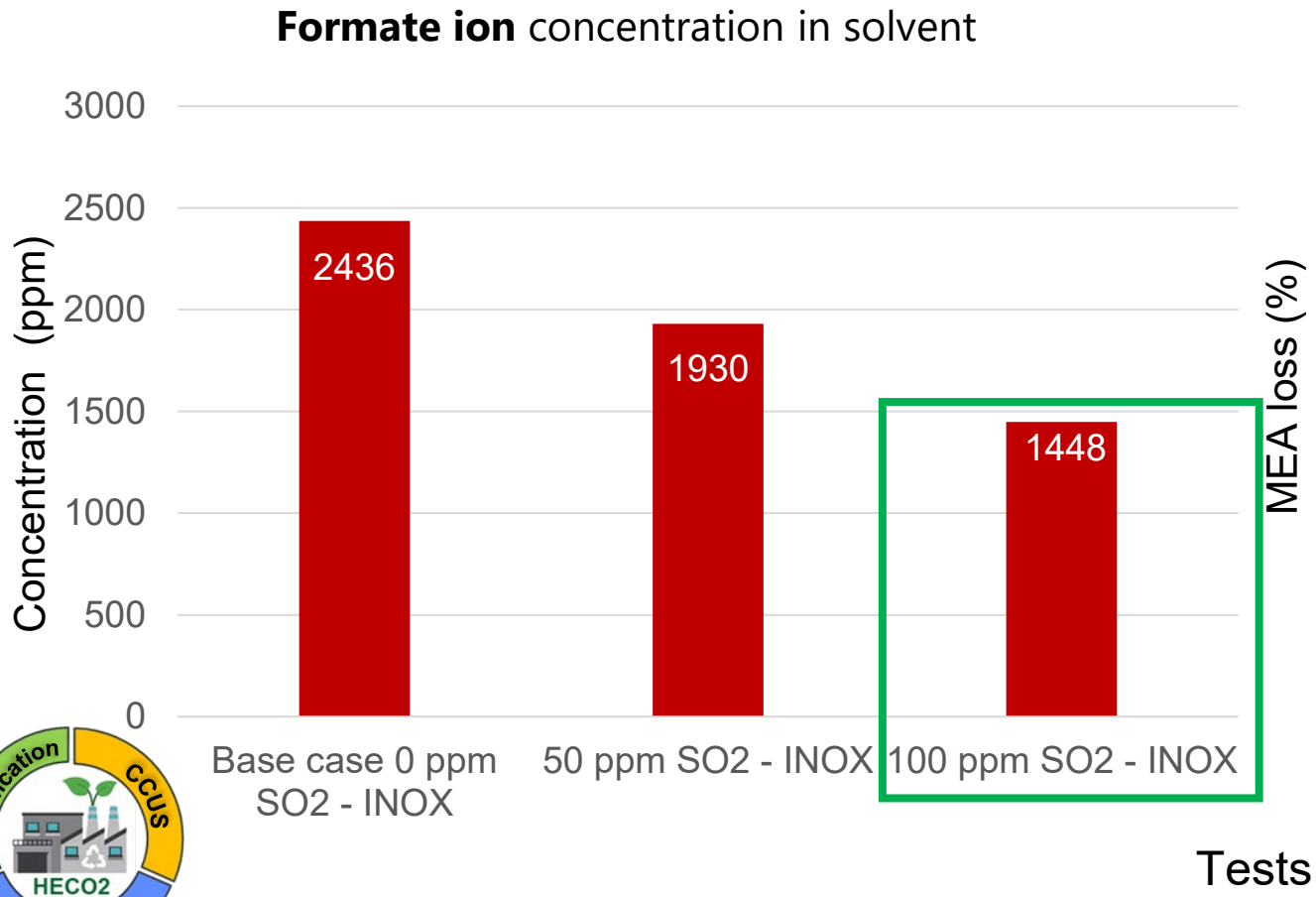


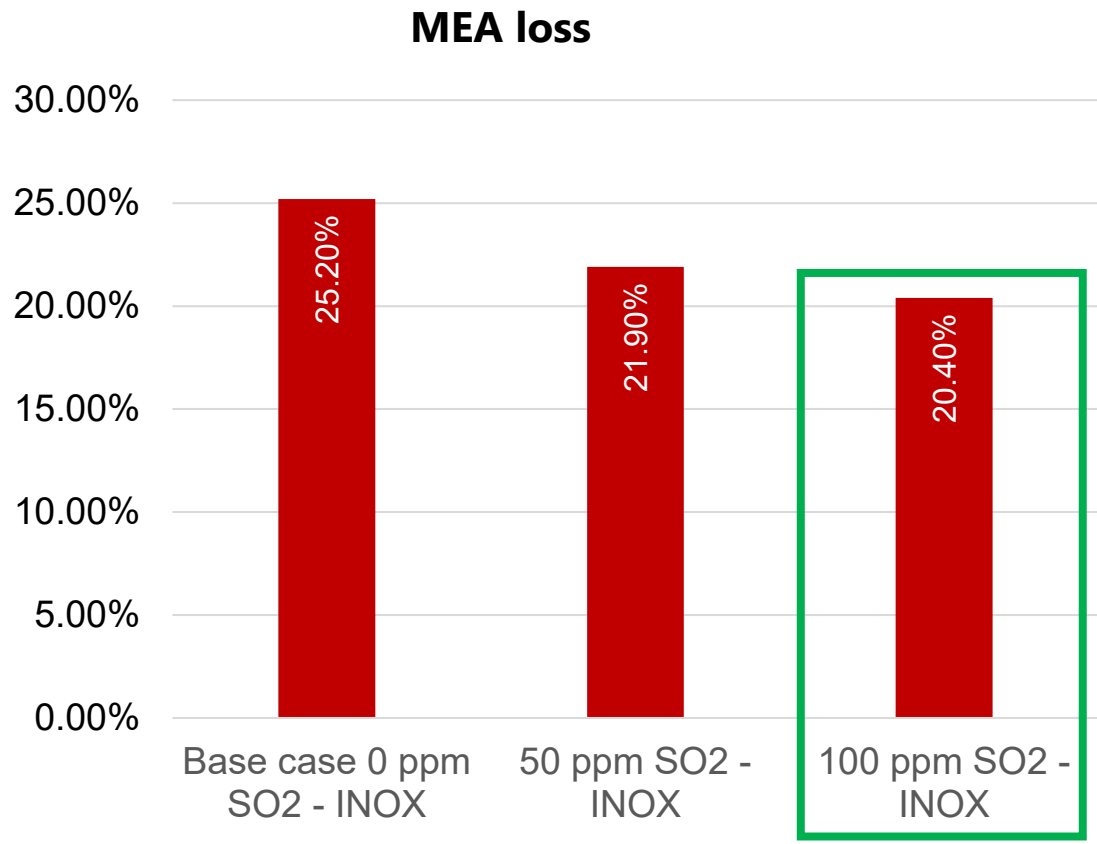


[2]IC measurement through collaboration with ENGIE Laborelec

Results

- IC² & HPLC analysis for the **Stainless-Steel** reactor with O_2
  - 5 % O_2 – 15 % CO_2 – 0/50/100 ppm SO2



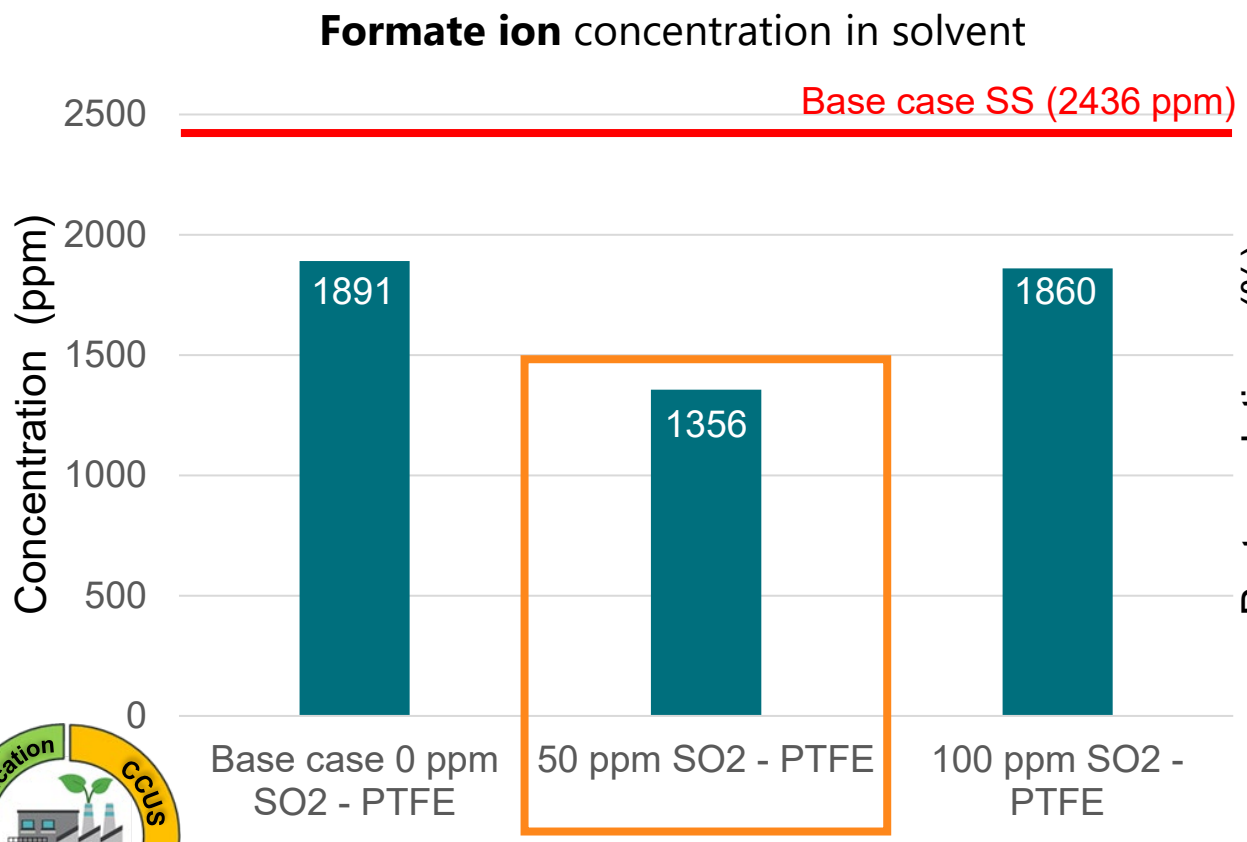


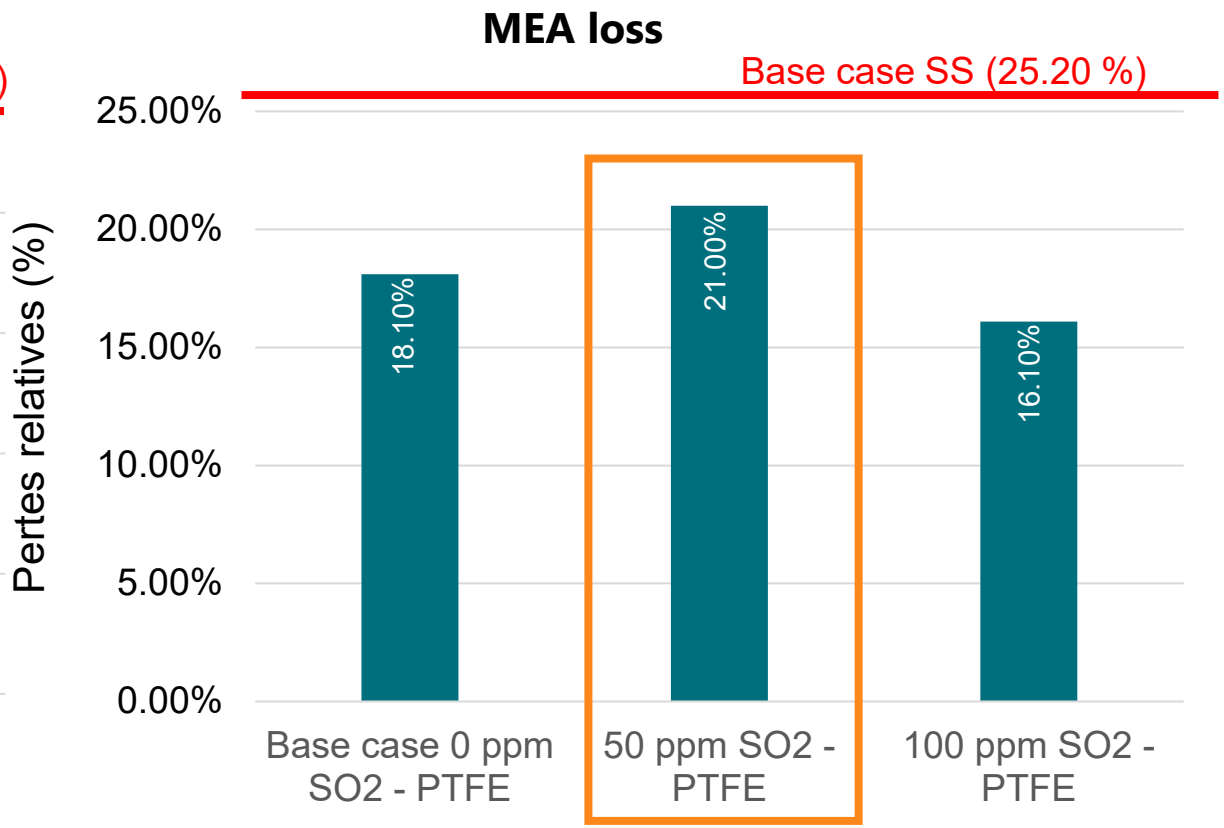
[2]IC measurement through collaboration with ENGIE Laborelec

Financé par l'Union européenne NextGenerationEU

Results

- IC² & HPLC analysis for the **PTFE** reactor with O_2
  - 5 % O_2 – 15 % CO_2 – 0/50/100 ppm SO2



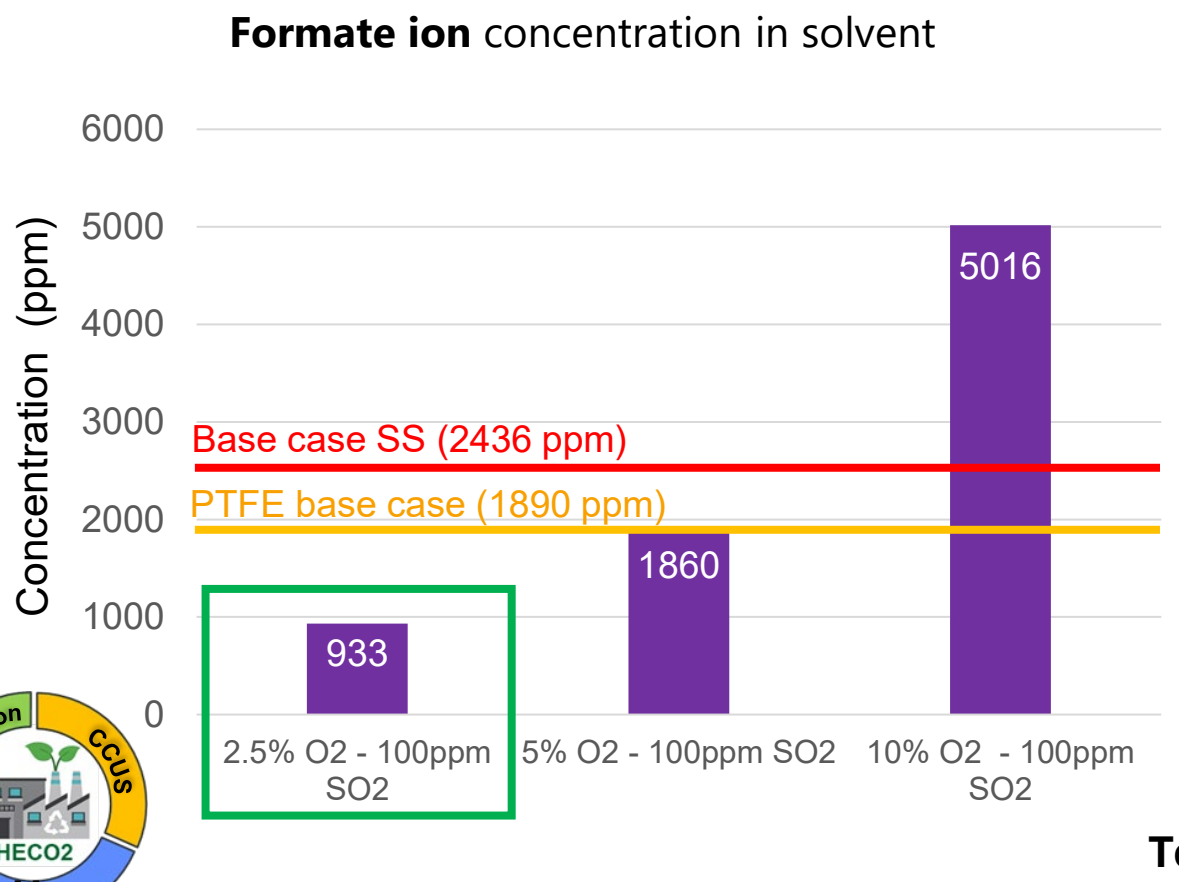


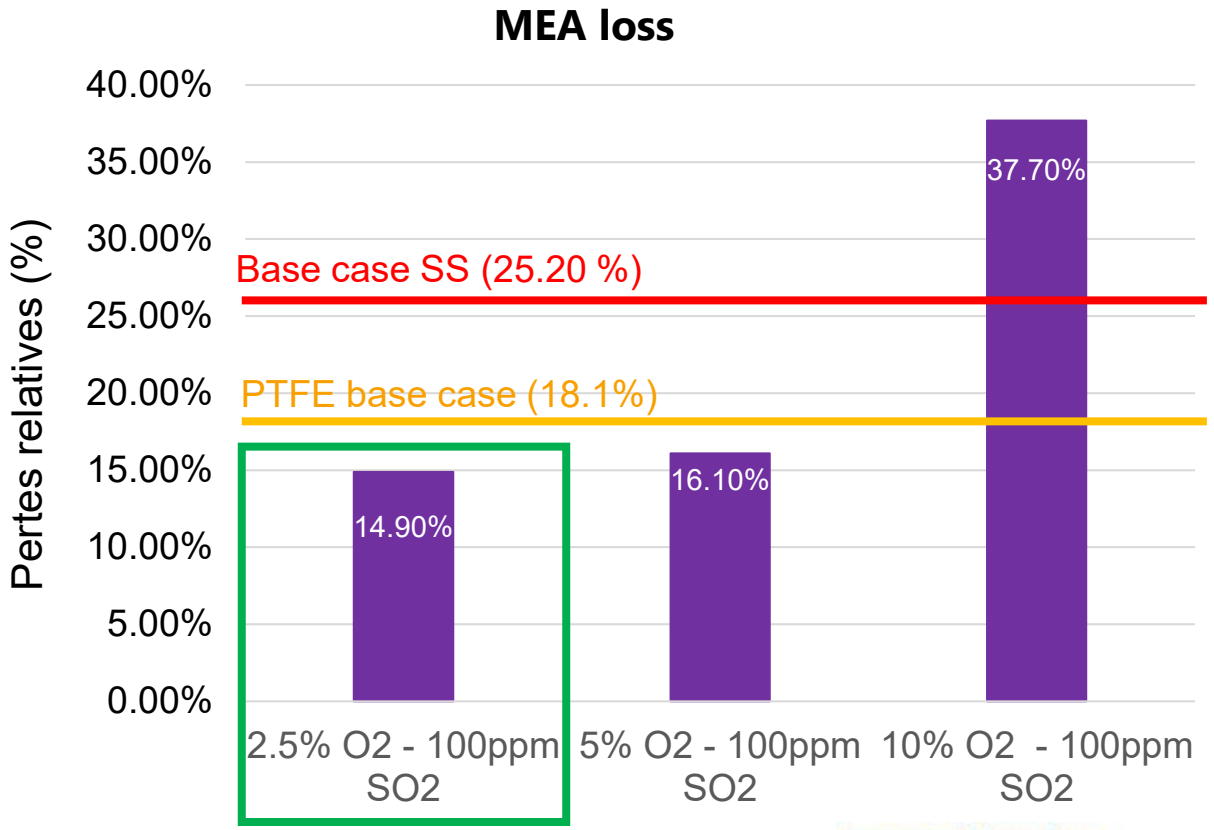
[2]IC measurement through collaboration with ENGIE Laborelec

Financé par l'Union européenne NextGenerationEU

Results

- IC² & HPLC analysis for the **PTFE** reactor with O_2
  - **2.5 - 10 %** O_2 – 15 % CO_2 – 100 ppm SO2





[2]IC measurement through collaboration with ENGIE Laborelec

Conclusion

- SO_2 degradation tests

  - The **PTFE** reactor leads to reduced MEA losses and lower formation of degradation ions ($HCOO^-$) compared to the **Stainless-Steel** reactor.

  - SO_2 appears to exert a protective effect against MEA degradation and the formation of $HCOO^-$ ions, apart from one test at 50 ppm, which should be repeated.

  - Increasing the O_2 concentration in the gas phase clearly promotes higher levels of degradation.

Financé par l'Union européenne NextGenerationEU

Further Work

- Other analysis
  - ICP-OES for Fe, Cu, Mn, Ni → corrosion and catalyst impact
  - Sulfate measurement & analysis → HSS formation
  - GC-FID for special degradation compounds → comparison with ternary mixture system
- Tests with higher [SO_2]
  - 200 ppm in both reactor → 3 different points for each case (protective effect vs corrosion)
  - Varying SO_2 concentration with 2.5 and 10 % O_2
- Modelling work with inclusion of SO_2 reactions in a validated CO_2 capture model including oxidative and thermal degradation
- Test of other solvent (e.g., CESAR1) → SolveMORE project

Financé par l'Union européenne NextGenerationEU

LIÈGE université
Chemical Engineering

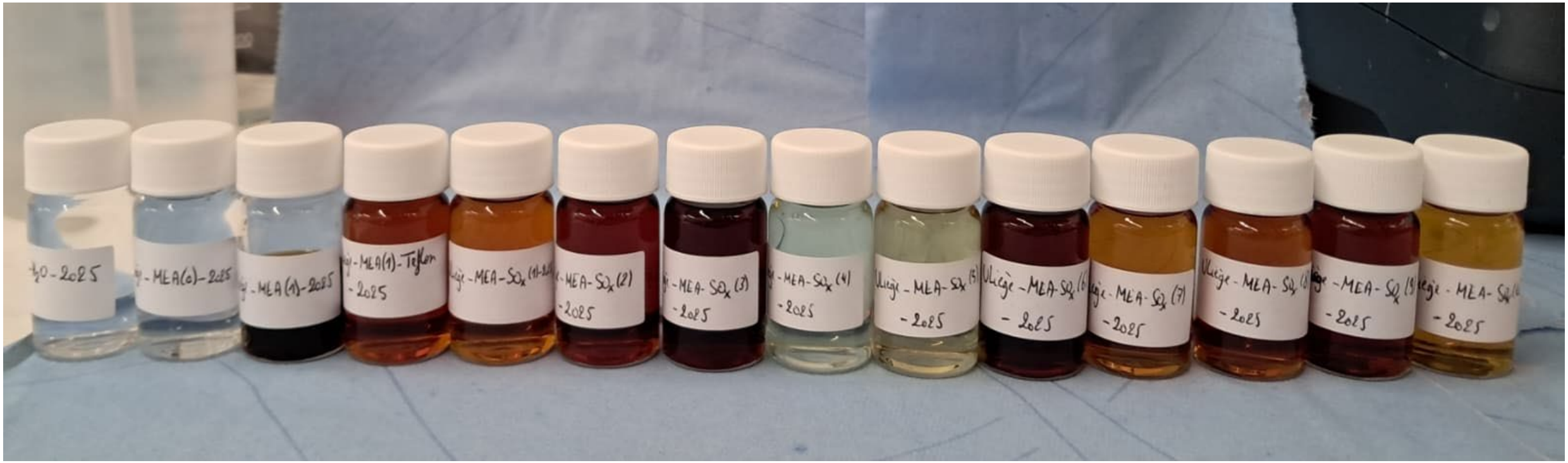
PEPs
CHEMICAL
ENGINEERING

Thank you for your attention!

Loris Baggio
Grégoire Léonard

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

Illustration of degraded samples



Degradation of Amine Solvent

- Reactions of MEA with flue gas contaminants (SO_x)
  - 2 main reactions are identified
    - SO_4^{2-} formation (condensed version) : SO_2 + ½ O_2 + 3 H_2O → SO_4^{2-} + 2 H_3O^+

Less O_2 available for oxidative degradation

Acidification

    - More complete version :

$$SO_{2(g)} \longrightarrow SO_{2(aq)}$$

$$SO_{2(aq)} + H_2O_{(aq)} \longrightarrow H_2SO_{3(aq)}$$

$$H_2SO_3 \longrightarrow H^+_{(aq)} + HSO_3^-{}_{(aq)}$$

$$HSO_3^-{}_{(aq)} \longrightarrow H^+_{(aq)} + SO_3^{2-}{}_{(aq)}$$

$$2SO_3^{2-}{}_{(aq)} + O_{2(g)} \longrightarrow 2SO_4^{2-}{}_{(aq)}$$

Degradation of Amine Solvent

- Thermal degradation studies (G. Léonard 2009-2013)
  - Batch degradation reactors
    - 3 weeks at 140 °C of loaded MEA 30 wt.-% solvent
    - Influence of temperature and CO_2 has been quantified
    - Influence of oxidative degradation inhibitors on MEA thermal degradation with CO_2
  - Almost no degradation could be observed in the absence of CO_2.
  - In the presence of CO_2
    - Small degradation of MEA observed at 120°C
    - Significant MEA degradation is observed at 140°C.
  - HEIA is the main thermal degradation product of MEA.
  - Dissolved metals (Fe, Cr, Ni, Mn) do not influence the thermal degradation of MEA with CO_2, independently of the presence of CO_2

Degradation of Amine Solvent

- **Thermal Degradation Tests**
  - MEA 30 wt.-% solvent prepared in lab and loaded with CO_2 until ~0.5 mol CO_2/mol MEA
    - Comparison between two methods (G. Léonard[1] & L. Braakhuis[2])
      - Tests on 3 weeks with intermediate samples each week (100g of loaded MEA solvent at 140 °C)
        - Cooling down before sampling & putting back in the oven for G. Léonard method
          - 1 cylindrical vessel for the entire test in the case of G. Léonard
        - Removing 1 cylindrical vessel each week
          - 3 cylindrical vessels for the entire test in the case of L. Braakhuis

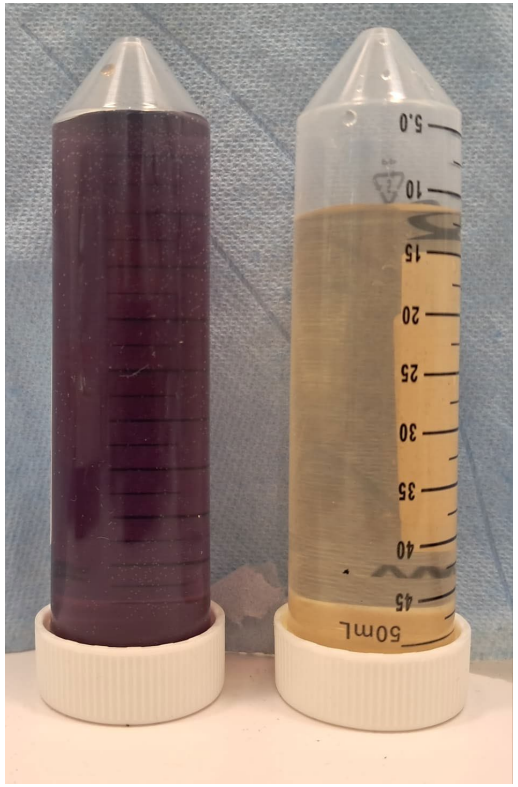
[1]G. Léonard, 'Optimal design of a CO2 capture unit with assessment of solvent degradation', PhD Thesis, Université de Liège, Liège, 2013. Accessed: Sept. 12, 2023. [Online]. Available: https://orbi.uliege.be/handle/2268/152320
[2]L. Braakhuis, 'Development of Solvent Degradation Models for Amine- Based CO2 Capture', PhD Thesis, Norwegian University of Science and Technology, Trondheim, 2024. [Online]. Available: https://ntnuopen.ntnu.no/ntnu-xmlui/handle/11250/3118629

Degradation of Amine Solvent

Thermal Degradation Tests

- First qualitative result (10th of September 2025) after 3 weeks

3 weeks non-stop at 140 °C



3 weeks with intermediate sampling each week (cooling down to ambient temperature)

Intermediate sampling will affect the presence of CO_2 in the solvent?