Carbon Management and Oil and Gas Research Project Review Meeting
Point Source Capture — Lab, Bench, and Pilot-Scale Research,
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# LAUNCH – International Collaboration on amine oxidation with results from Niederaussem

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# We must understand and mitigate amine oxidation

2G amine scrubbing is & will be the dominant technology to address $CO_2$ emissions from point sources.

- Power grids will require fossil fuel for reliability.
- No 3G capture technology will be significantly better.

Oxidation is a significant environmental & economic risk in the deployment of 2G amine scrubbing

- What are we going to produce and emit?
- What are its health & safety impacts?
- How much will it cost to mitigate impacts and replace solvent?

Major vendors still view oxidation as a major issue

- Initial degradation issues at Boundary Dam have not resolved?
- ION is developing ICE 31 to provide greater resistance
  - to oxidation at greater flue gas oxygen
- MHI is developing KS-2; it has greater stability than KS-1.

# Three important oxidation mechanisms

- 1. $NO_2$ oxidizes all amines at 0.2 to 5 ppm in the flue gas
- 2. Dissolved oxygen oxidizes amines at elevated T before the stripper
- 3. $Fe^{+3}$ oxidizes amines at stripper T and is regenerated from $Fe^{+2}$ in absorber

- Amine selection is an important task of the developers. It will be important as some amines are more resistant to these mechanisms than others.

# The LAUNCH Project, an international collaboration

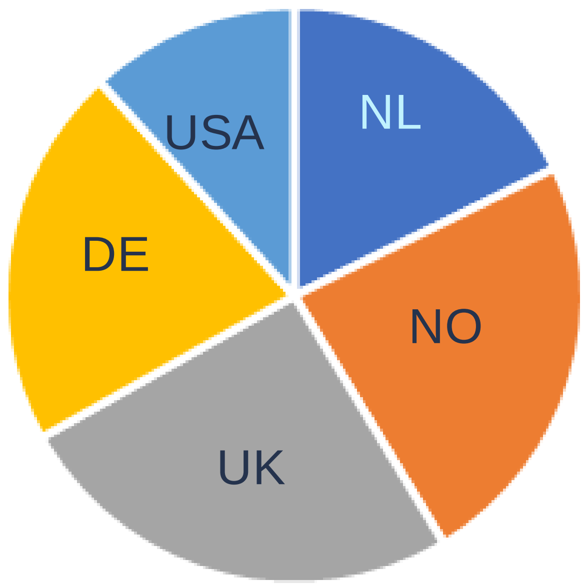
## Lowering Absorption process UNcertainty, risks and Costs by predicting and controlling amine degradation

- 11 partners from 5 countries

RWE
Los Alamos NATIONAL LABORATORY EST. 1943
TxCMP
TNO innovation for life
NTNU
SINTEF
The University Of Sheffield.
THE UNIVERSITY OF EDINBURGH
DOOSAN
biobe
AVR.

- Total budget: € 7.2 million
- Total funding: € 5.1 million

Total Budget per Country



# LAUNCH Objectives

## Main Objective:

Accelerate the implementation of $CO_2$ capture in various industries and support the development and qualification of novel solvents by establishing a fast-track, cost-effective de-risking mechanism to predict and control degradation of capture solvents.

Sub-obj #1: Developing the ability to predict degradation of (novel) CO2 capture solvents

Degradation database and a generalized degradation network model

Sub-obj #2: Developing strategies to control degradation, minimizing solvent loss and therefore the environmental impacts of CO2 capture

Degradation management strategies to include optimized process design, flue gas pre-treatment, and the removal of oxygen and iron from the solvent.

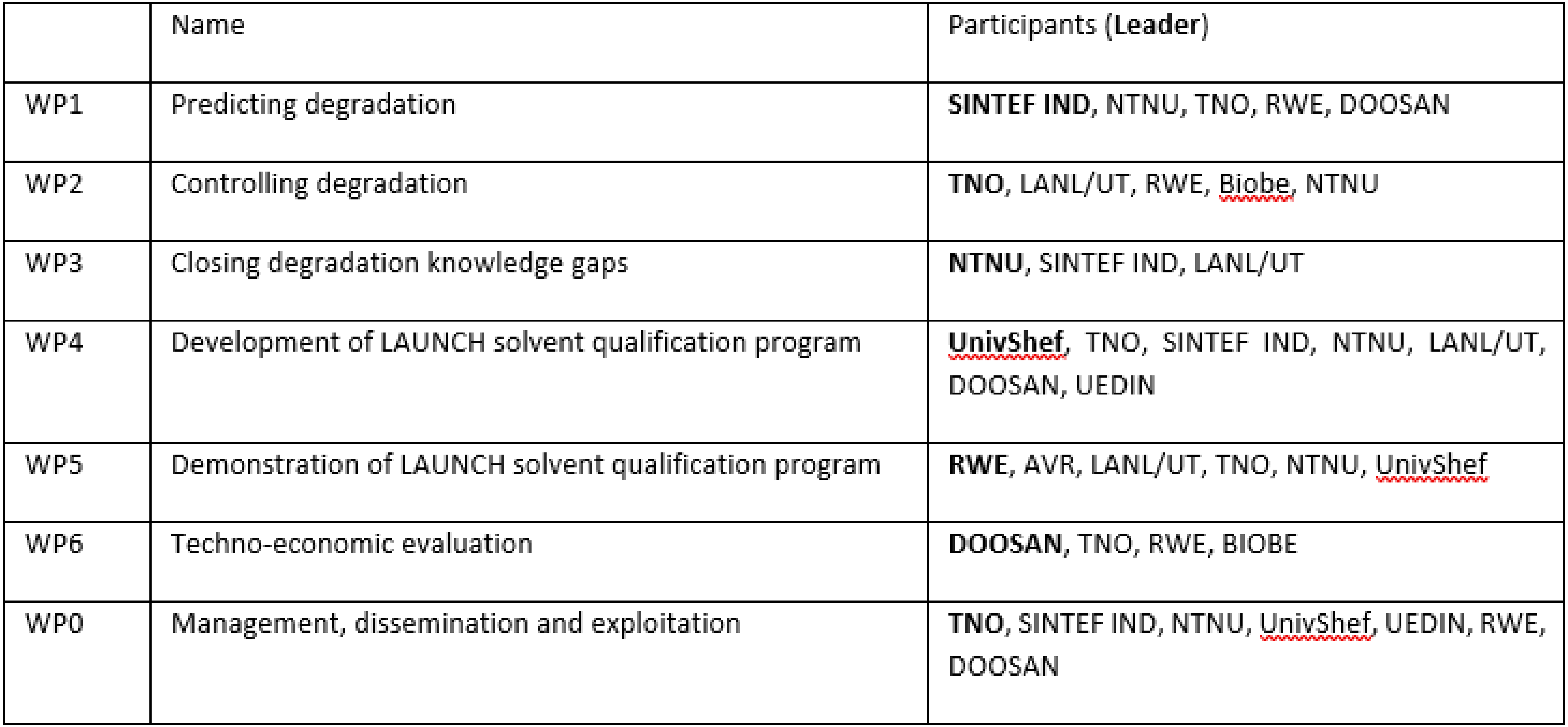
Sub-objective #3: Developing and demonstrating the LAUNCH solvent qualification program

Reduce testing time and scale

## Build the LAUNCH Solvent Development Protocol

Guidelines, test protocols, design of the LAUNCH test rig.

# LAUNCH – Work Packages



| | Name | Participants (**Leader**) |
|---|---|---|
| WP1 | Predicting degradation | **SINTEF IND**, NTNU, TNO, RWE, DOOSAN |
| WP2 | Controlling degradation | **TNO**, LANL/UT, RWE, Biobe, NTNU |
| WP3 | Closing degradation knowledge gaps | **NTNU**, SINTEF IND, LANL/UT |
| WP4 | Development of LAUNCH solvent qualification program | **UnivShef**, TNO, SINTEF IND, NTNU, LANL/UT, DOOSAN, UEDIN |
| WP5 | Demonstration of LAUNCH solvent qualification program | **RWE**, AVR, LANL/UT, TNO, NTNU, UnivShef |
| WP6 | Techno-economic evaluation | **DOOSAN**, TNO, RWE, BIOBE |
| WP0 | Management, dissemination and exploitation | **TNO**, SINTEF IND, NTNU, UnivShef, UEDIN, RWE, DOOSAN |

# Objectives WP5: Demonstrating the solvent qualification programme

- **Task 5.1 - Validation of the LAUNCH rigs at RWE and AVR**

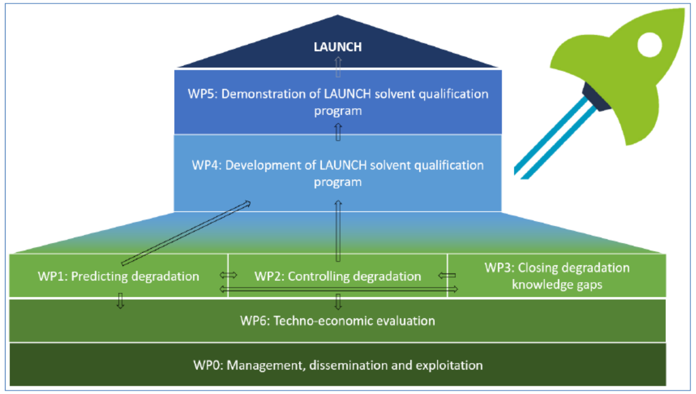
  validation of reliable **prediction of the degradation** behaviour of different classes of solvents by the LAUNCH rig technology

- **Task 5.2 - Demonstration of degradation control technologies at RWE and NCCC**

  demonstration of the performance of **degradation control measures** with different effect mechanisms

- **Task 5.3 - Demonstration of solvent qualification program for second generation solvents at PACT**

  evaluation of the effectiveness of **solvent management** under the conditions of **accelerated degradation**



LAUNCH

WP5: Demonstration of LAUNCH solvent qualification program

WP4: Development of LAUNCH solvent qualification program

WP1: Predicting degradation

WP2: Controlling degradation

WP3: Closing degradation knowledge gaps

WP6: Techno-economic evaluation

WP0: Management, dissemination and exploitation

RWE's pilot plant, Niederaussem, lignite, 0.3 $t_{CO2}$/h

AVR's capture plant, Duiven waste incineration, 12 $t_{CO2}$/h

NCCC test facility, Alabama hard coal, 0.4 $t_{CO2}$/h

PACT test facility, Sheffield natural gas/biomass, 0.04 $t_{CO2}$/h

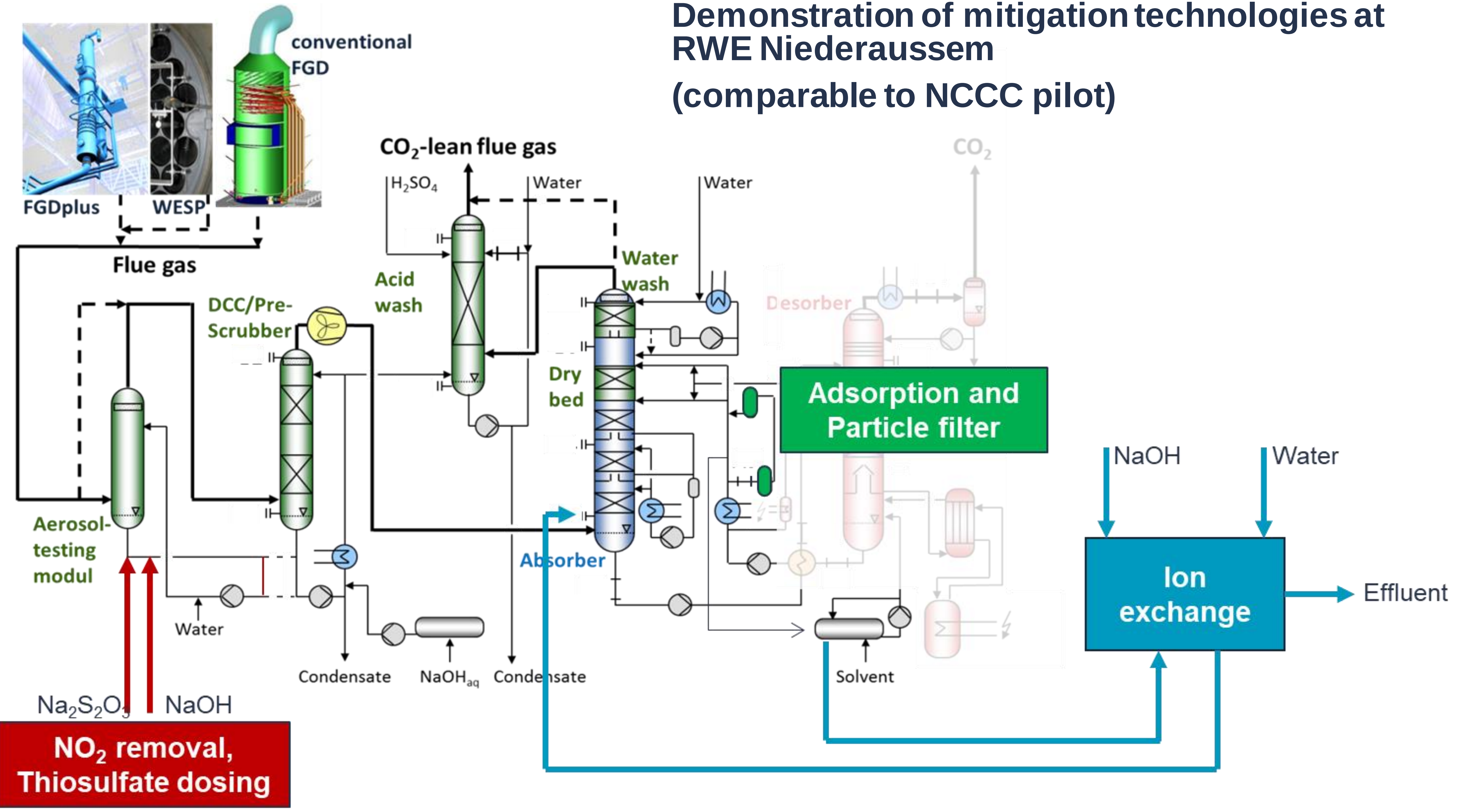
**Sites of technology demonstration**

**The LAUNCH WP5-Team:**

RWE AVR. Los Alamos NATIONAL LABORATORY NTNU Norwegian University of Science and Technology TxCMP THE UNIVERSITY of EDINBURGH The University Of Sheffield. TNO innovation for life

# Demonstration of mitigation technologies at RWE Niederaussem

# (comparable to NCCC pilot)

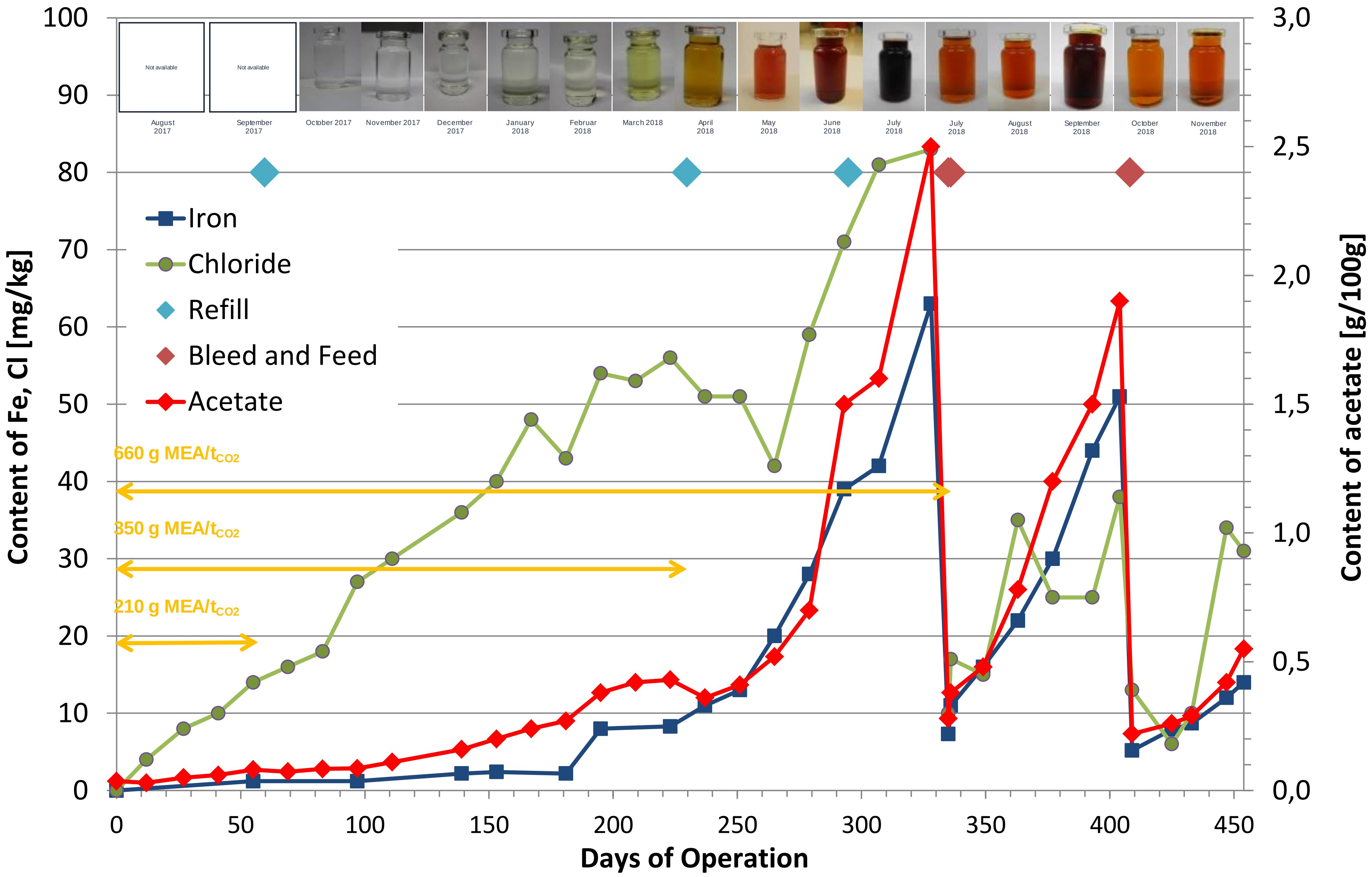


**Adsorption and Particle filter**

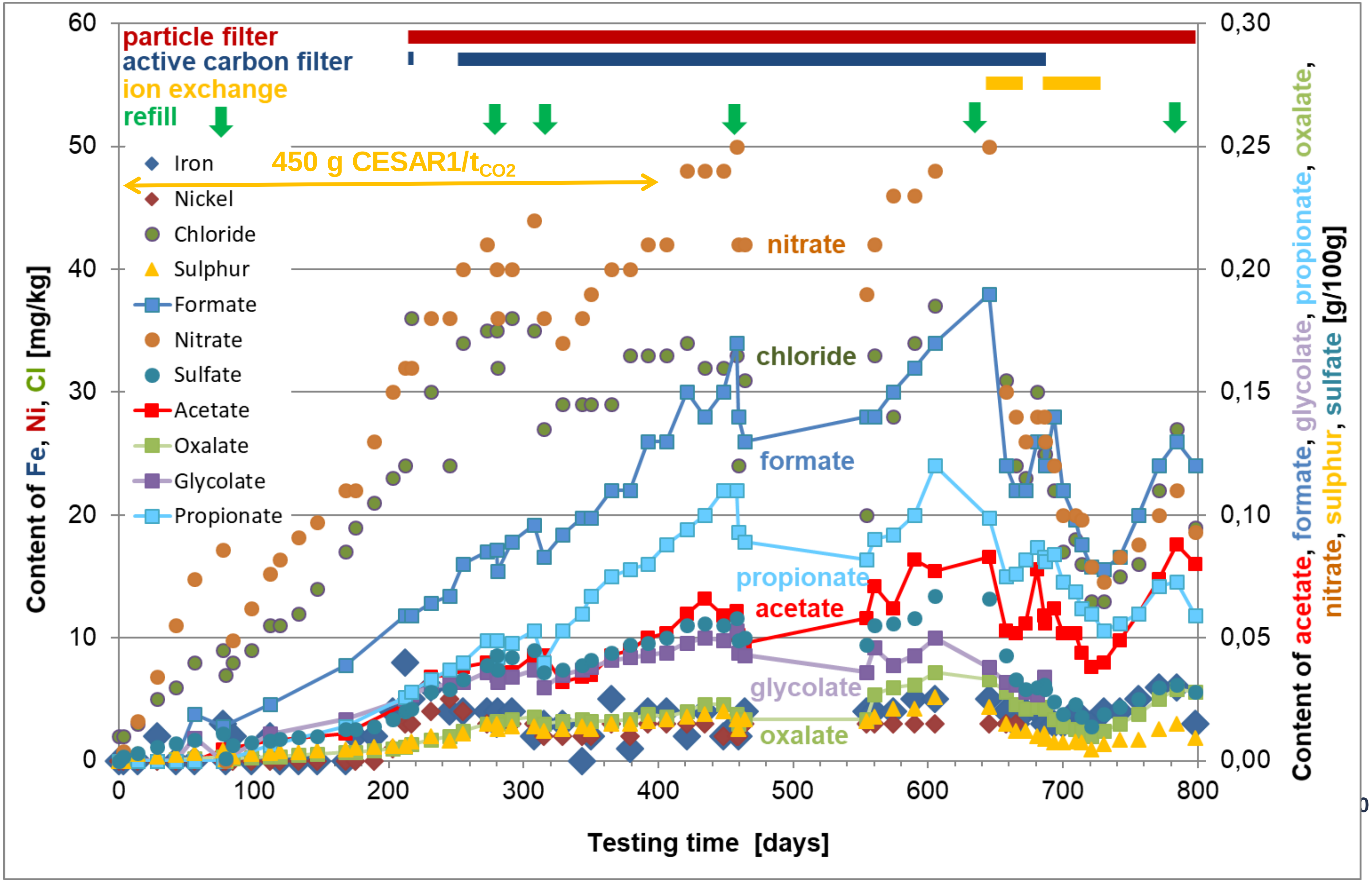
**Ion exchange**

**$NO_2$ removal, Thiosulfate dosing**

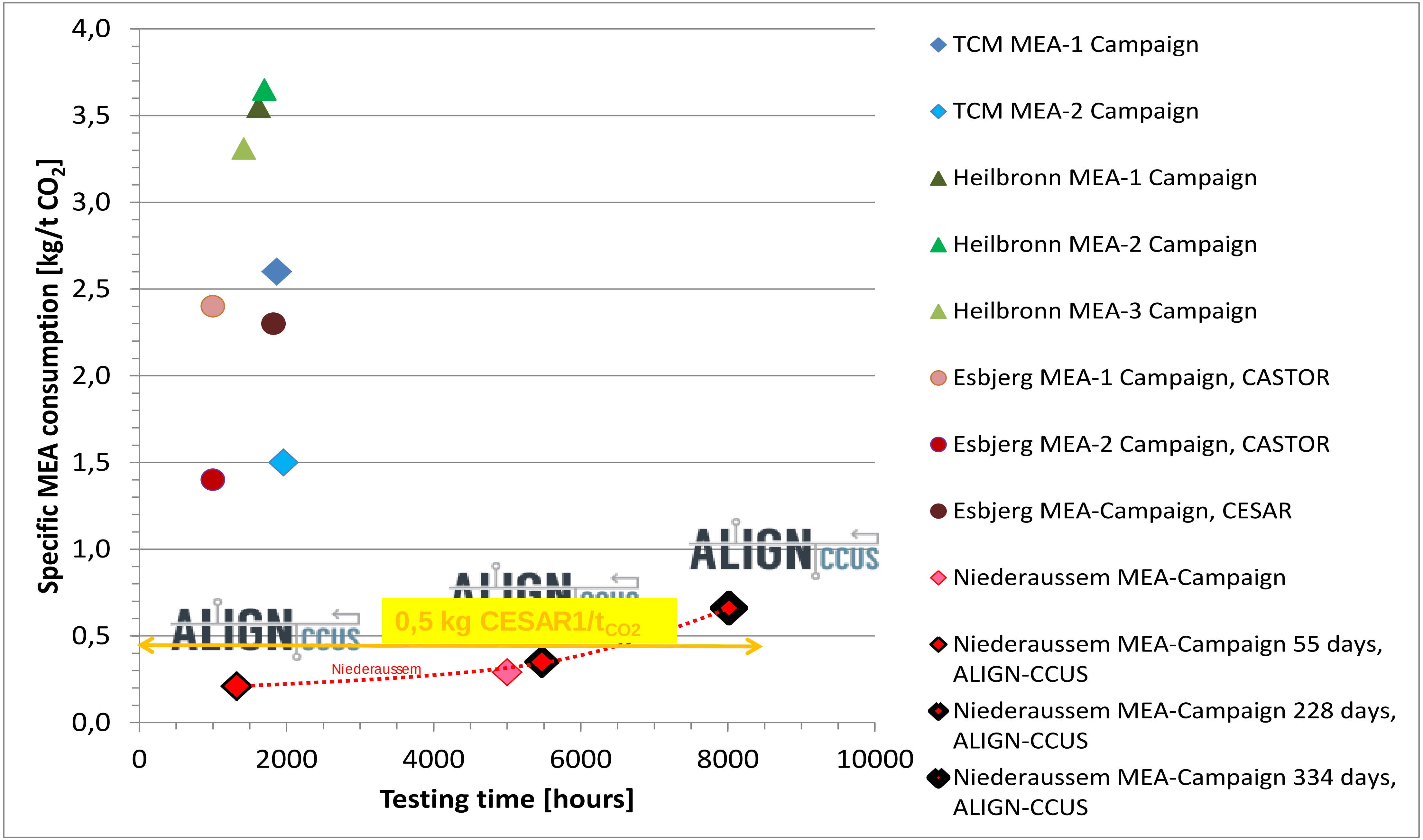
# MEA degradation at Niederaussem



# Cesar-1 (27% AMP+13% PZ) degradation at the Niederaussem pilot



# Amine consumption in various pilot campaigns



# PZ oxidation by $NO_2$ (Fine, 2015)

- **In Absorber (low T, minor)**

  $NO_2 + PZ \rightarrow PZ\bullet + NO_2^-$ (Free radical absorption)

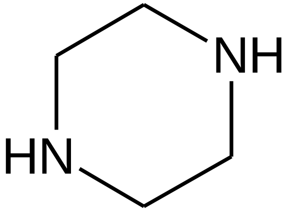
  $2PZ\bullet \rightarrow PZOH + PZ$ (major)

- **In Stripper (high T, dominates)**

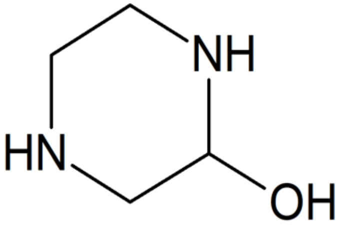
  $NO_2^- + PZCOOH \rightarrow MNPZ + HCO_3^-$

  $MNPZ \xrightarrow{\Delta,\, base} PZOH + N_2O$

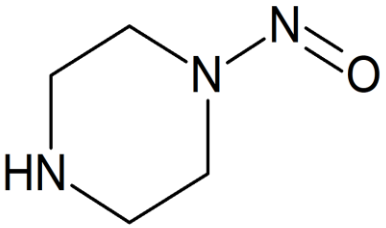
- **Stoich:** $NO_2 + 1.5\ PZ \rightarrow 1.5\ PZOH + 0.5\ N_2O$



PZ



PZOH



MNPZ

# PZ oxidation by $NO_2$ (catalytic hypothesis)

☐ **In Absorber (low T, minor)**

$NO_2 + PZ \rightarrow PZ\bullet + NO_2^-$ (Free radical absorption)

$\mathbf{PZ\bullet} + O_2 \rightarrow PZOO\bullet$

$PZOO\bullet + PZ \rightarrow \mathbf{PZ\bullet} + PZOOH$

**Chain reaction**

$2\ \mathbf{PZ\bullet} + H_2O \rightarrow PZ + PZOH$ (Termination)

$PZOOH + PZ \rightarrow 2PZOH$

☐ **In Stripper (high T, dominates)**

$NO_2^- + PZCOOH \rightarrow MNPZ + HCO_3^-$

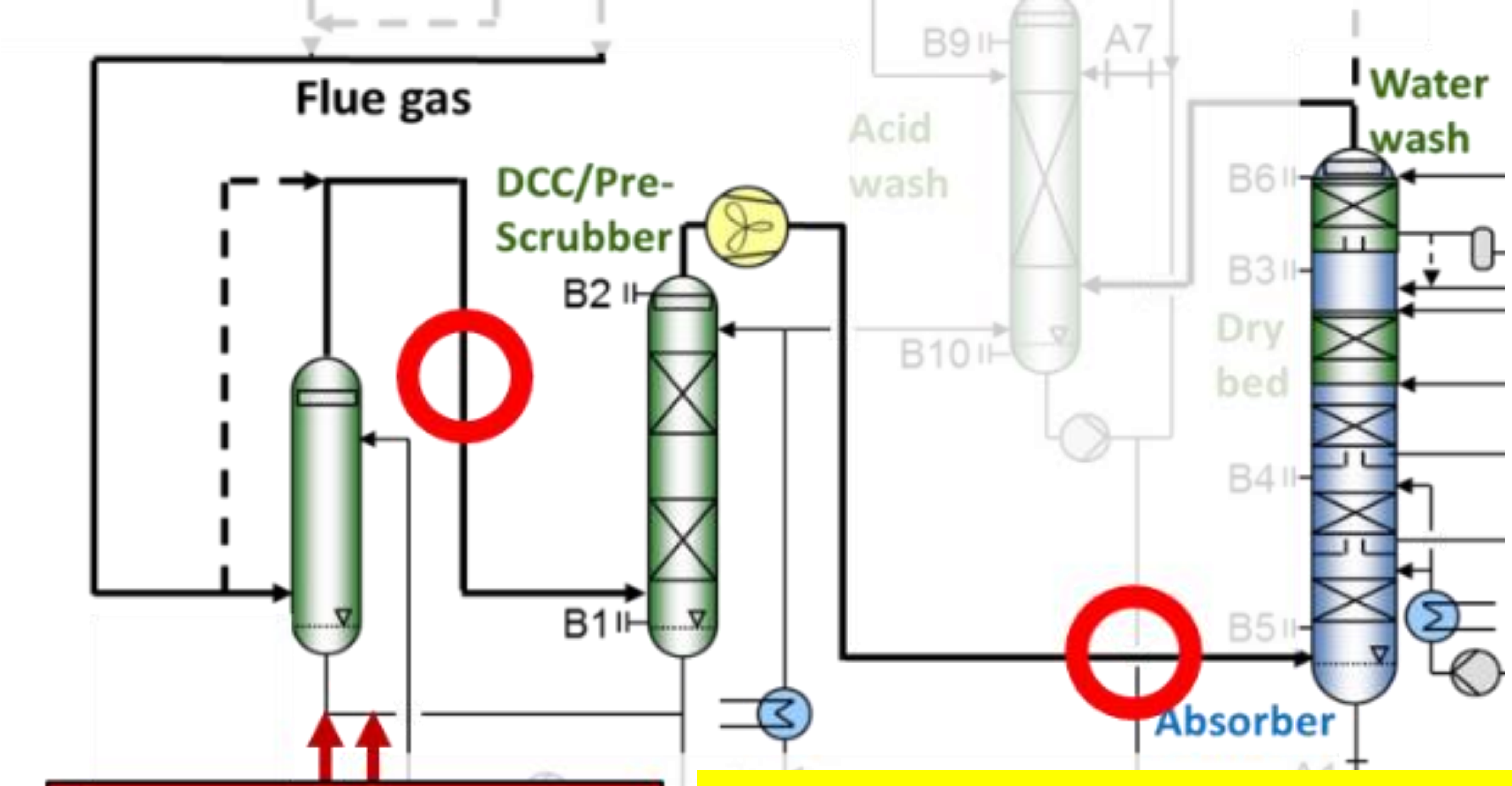
$MNPZ \xrightarrow{\Delta, base} PZOH + N_2O$

☐ **Sum:** $NO_2 + n\ PZ \rightarrow n\ PZOH$ + other products

# Removal of $NO_2$ from the flue gas by sulfite scrubbing with thiosulfate to inhibit sulfite oxidation: $NO_2 + SO_3^{=} \rightarrow NO_2^{-} + SO_3^{-}$

- Concept was successfully tested at NCCC at Wilsonville, Alabama, USA in 2017
- 90-95% $NO_2$ removal at pH> 8.5
  sulfite 0 - 70 mmol/kg; thiosulfate 0 - 240 mmol/kg;
  dosing into a separate column for $SO_2$ polishing with 20 ft of M 252Y
  - upstream of the direct contact cooler (DCC))

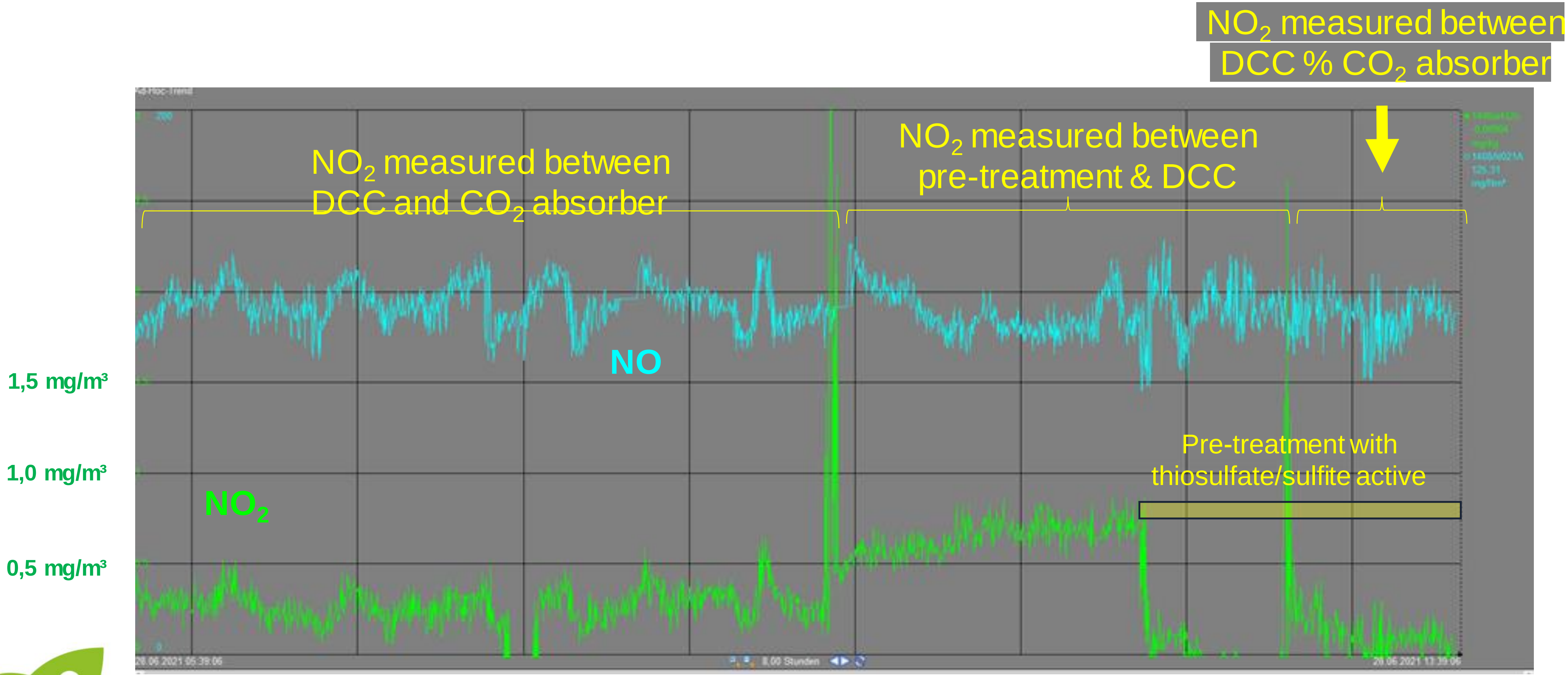
- **At Niederaussem dosing into turbulent spray scrubber loop**
- **Condensate formation by cooling the flue gas must be minimized (dilution and loss of active agents)**
- **pH values >8 might be critical for the material resistance**
- **Packing was added to get acceptable mass transfer**



$NO_2$ removal, thiosulfate dosing

Initial testing of thiosulfate was ineffective
Then added M602Y packing
& reduced water intrusion

# NO$_2$ Removed at Niederaussem by thiosulfate/sulfite dosing



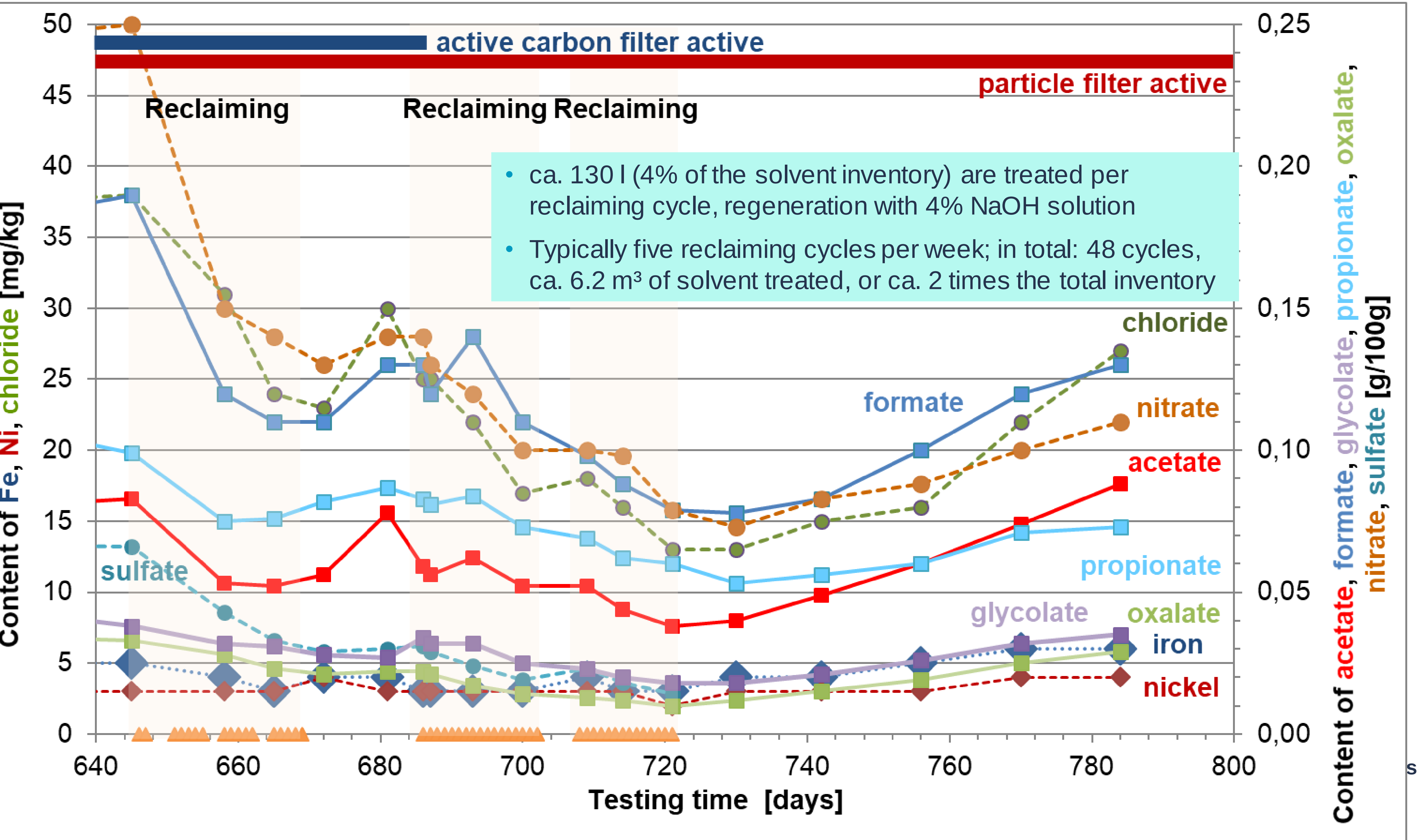
# Mitigate Oxidation by $Fe^{+3}$: Remove it from Cesar-1 by Anion Exchange

## Laboratory pre-testing of anionic and cationic ion exchange resins

**Analytical results for three metal cations from CESAR1 (aged for 645 days)**

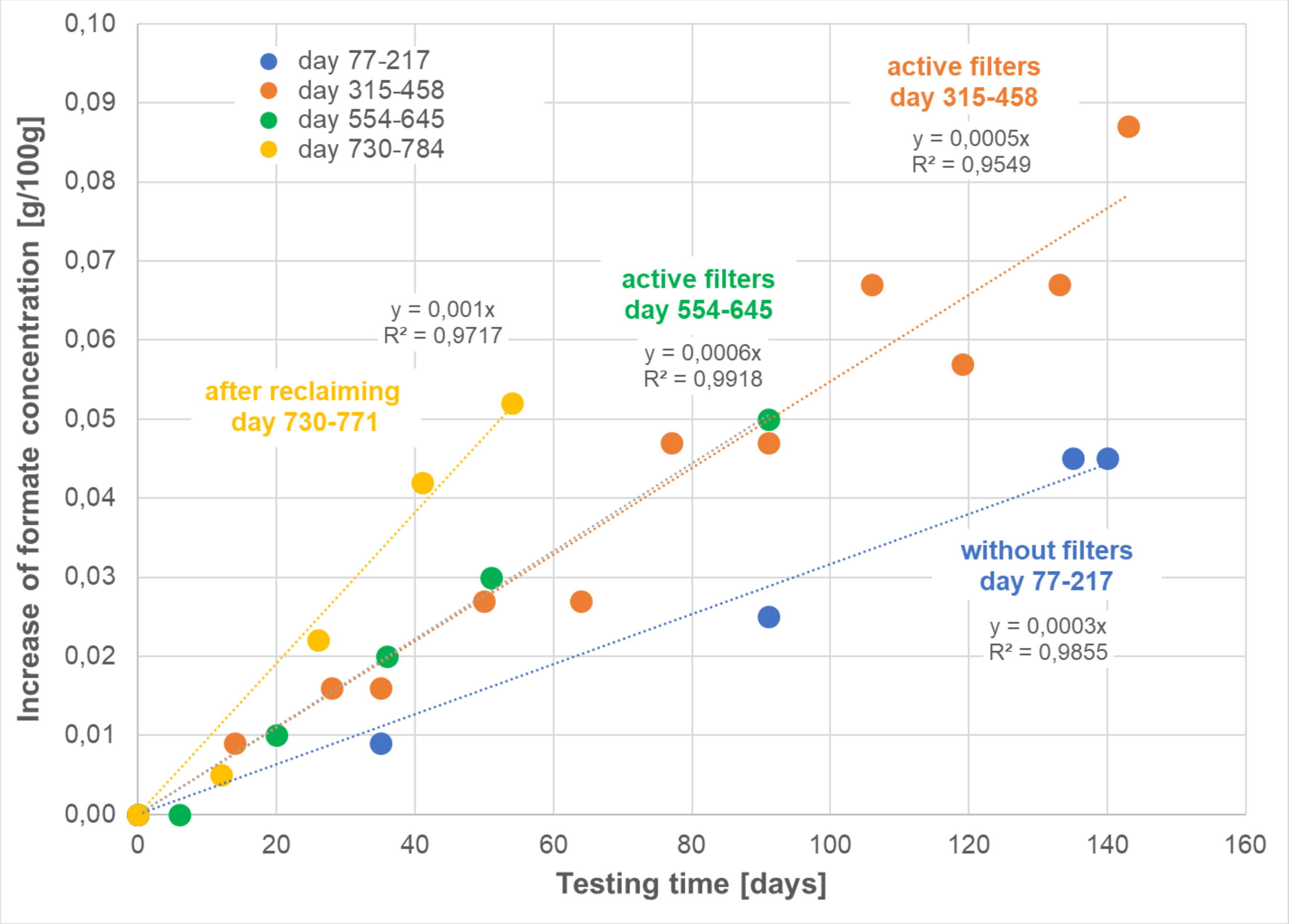
| | Fe [mg/l] | Ni [mg/l] | Zn [mg/l] |
|---|---|---|---|
| Untreated aged CESAR1 (benchmark) | 5.2 | 3.4 | 1.4 |
| Anionic resin (used in pilot plant) | 0.33 (94%) | 3.8 (0%) | 0.260 (81%) |
| Type A (cationic resin) | 1.7 (67%) | 1.5 (56%) | 0.003 (100%) |
| Type B (cationic resin) | 1.5 (71%) | 3.3 (3%) | 0.003 (100%) |
| Type C (cationic resin) | 5.1 (2%) | 2.6 (24%) | 0.440 (69%) |

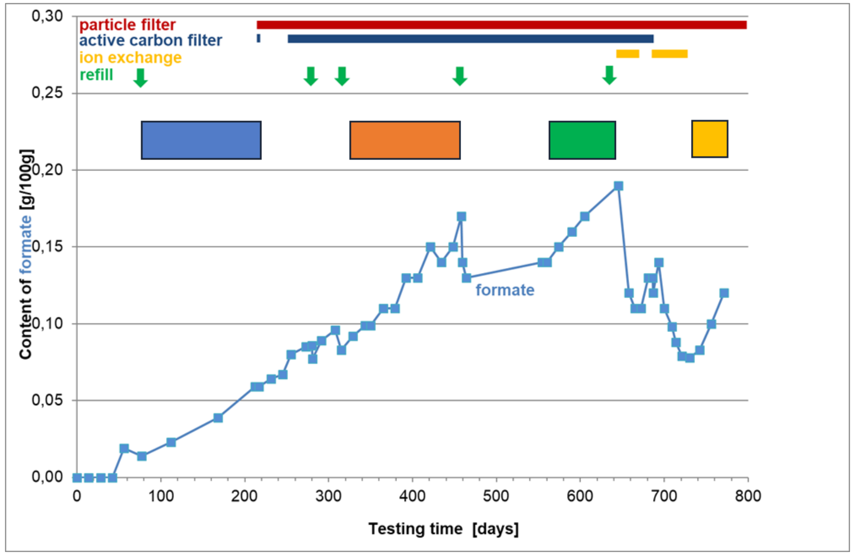
# Heat stable slats and dissolved Fe removed by anion-exchange reclaiming of CESAR1



- ca. 130 l (4% of the solvent inventory) are treated per reclaiming cycle, regeneration with 4% NaOH solution
- Typically five reclaiming cycles per week; in total: 48 cycles, ca. 6.2 m³ of solvent treated, or ca. 2 times the total inventory

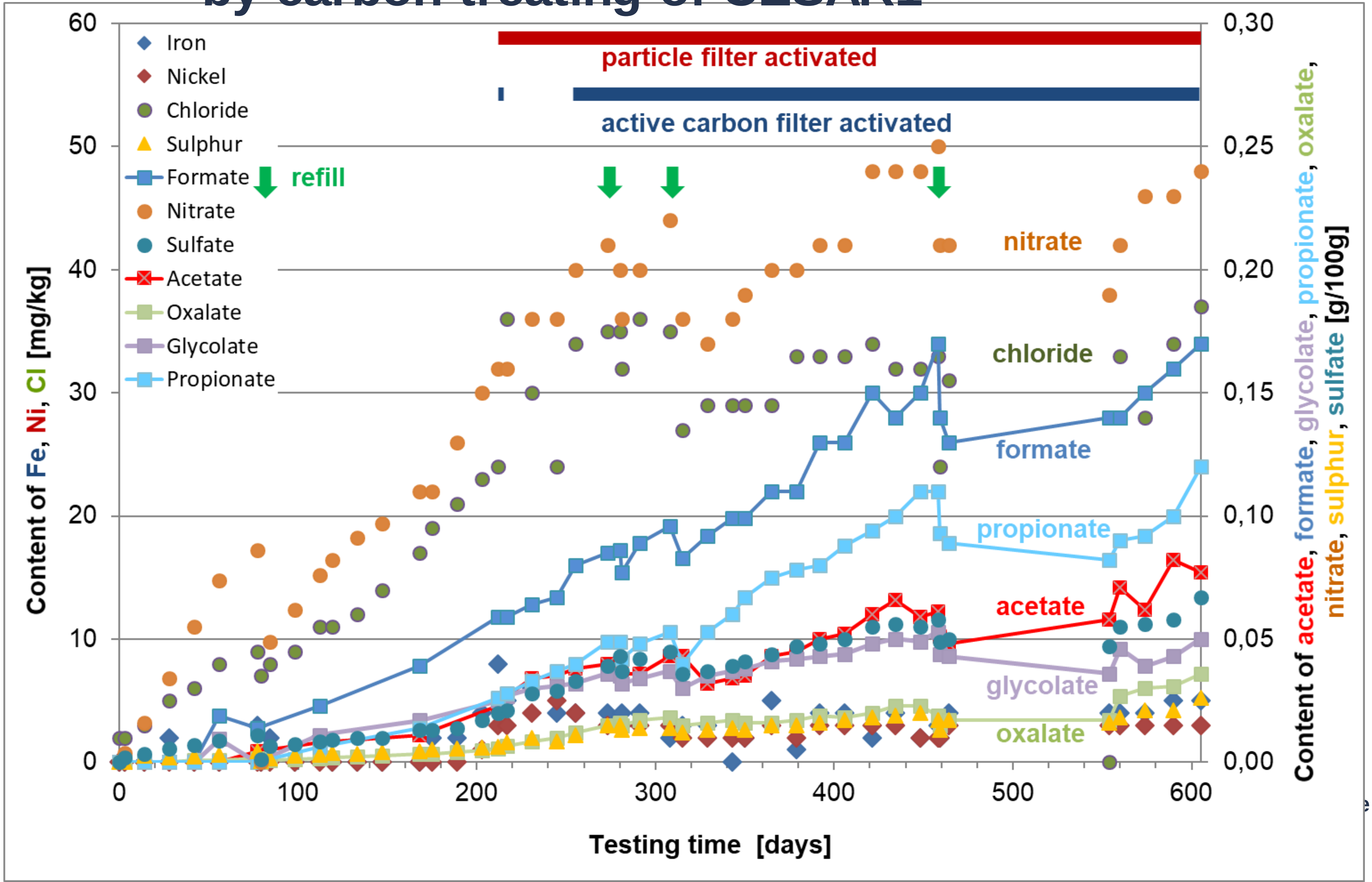
# Demonstration of reduced solvent degradation by ion-exchange-based reclaiming for CESAR1



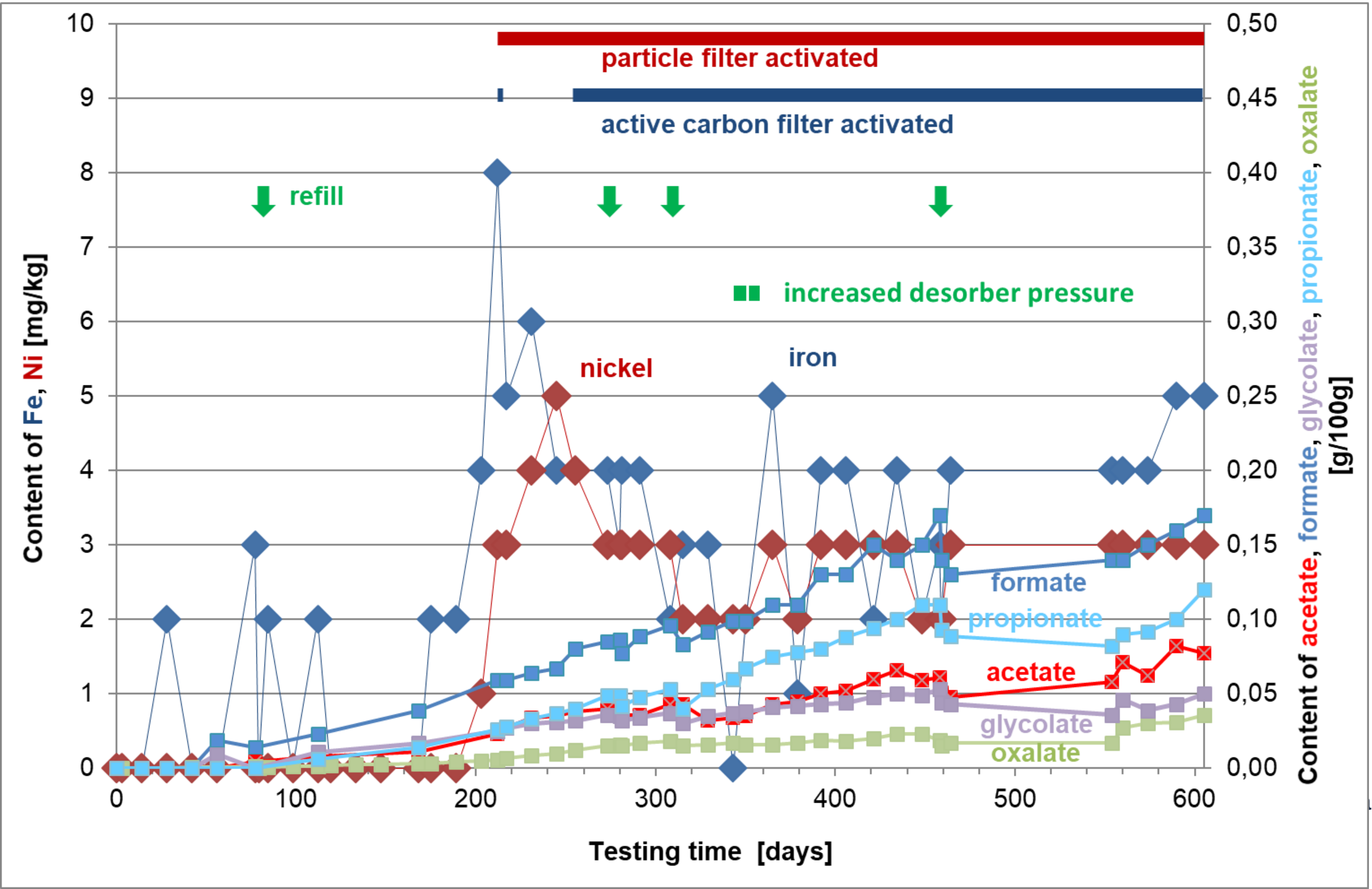


- **Removal of metals and oxidative degradation products and trace components does not necessarily mean a lower solvent degradation rate.**

# Demonstration of reduced solvent degradation by by carbon treating of CESAR1



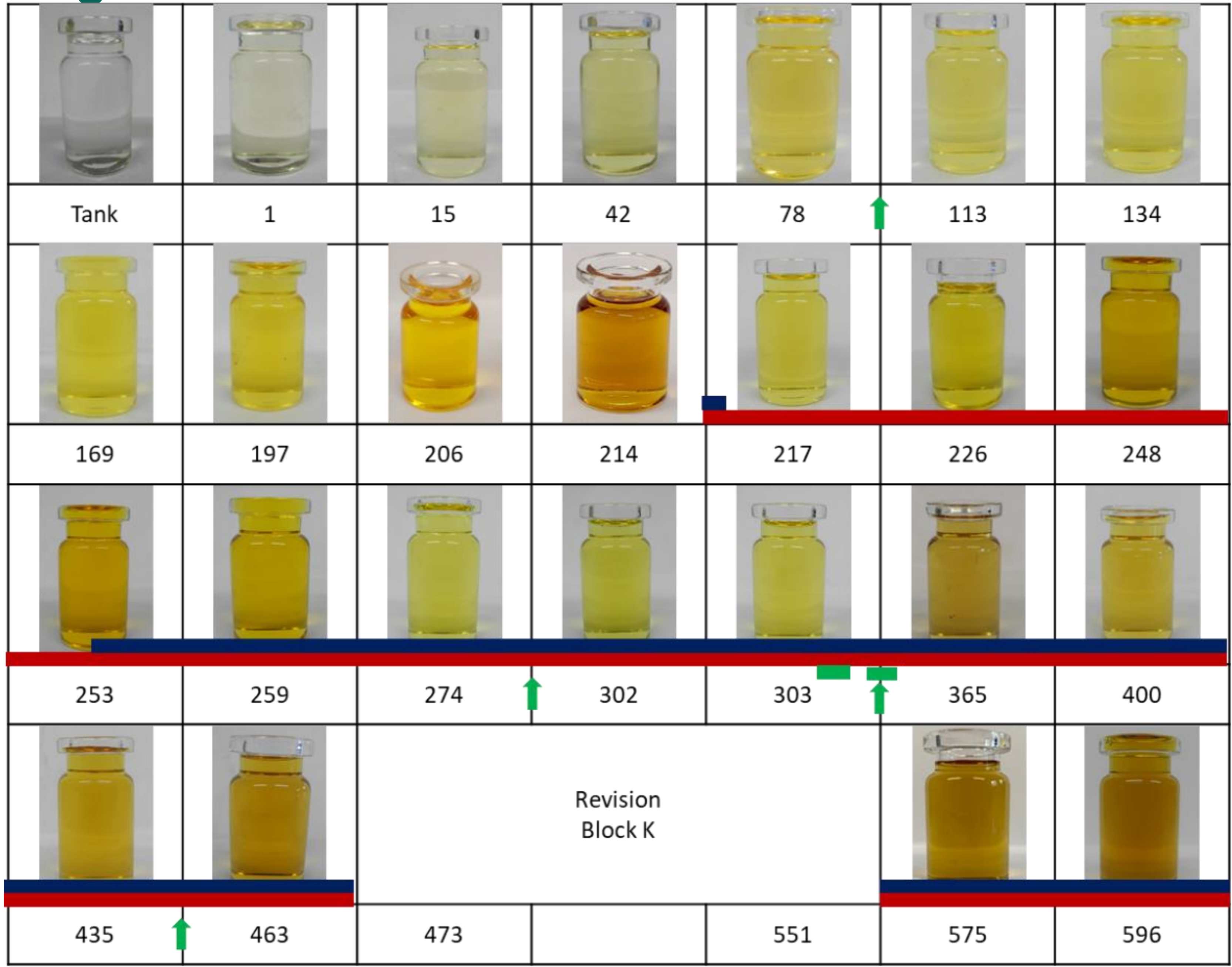
# Demonstration of reduced solvent degradation by adsorption of trace elements from CESAR1



- Active carbon filter & particle filter reduce the iron and nickel concentration in the solvent
- No explicit correlation between trace elements and solvent degradation visible
- No clear effect of the active carbon filter and the particle filter on degradation

# Carbon treating removes color in Cesar-1 at Niederaussen

Carbon filter on
Particle filter on



# Conclusions

1. Cesar-1 (AMP/PZ) oxidizes slower than MEA

2. Sulfite/thiosulfate prescrubbing can remove $NO_2$ if adequate packing is provided. Some additional $NO_2$ may be produced after this prescrubber.

3. Heat stable salts (formate) and dissolved iron were reduced by anion exchange, but the formate formation rate returned to the same trend after treating.

4. Carbon treating of Cesar-1 removed color and some dissolved iron, but did not appear to reduce degradation

# Future work on $NO_2$

1. Longer term testing of $NO_2$ removal at Niederaussem to determine if it reduces the degradation rate. (LAUNCH)
2. Testing with & without $NO_2$ addition to PZAS by the University of Texas (FE0031861)
    a. Bench-scale
    c. ASAP rig (small pilot)
    b. SRP pilot plant (air/$CO_2$)
    c. NCCC pilot plant (synthetic NGCC flue gas)

# Other and Future work on role & mitigation of $Fe^{+3}/Fe^{+2}$

LAUNCH at UT

$Fe^{+3}/Fe^{+2}$ solubility in PZ – Bench-scale testing at UT

$Fe^{+3}/Fe^{+2}$ removal at UT

- by sulfide precipitation
- by ion exchange

LAUNCH at TNO

- Metal–free rig built by BIOBE

FE003186 at UT (next presentation)

- $Fe^{+3}/Fe^{+2}$ removal from PZ by carbon treating

# Personal Acknowledgements

Peter van Os, TNO, Coordinator of LAUNCH, provided general slides on LAUNCH

Peter Moser, RWE Power, WP5 leader, provided slides for Niederaussem pilot plant results

# Acknowledgements

LAUNCH

Accelerating
CCS
Technologies

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