ACT LAUNCH Project No 299662

Lowering **A**bsorption process **UN**certainty, risks and **C**osts by predicting and controlling amine degradation

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Construction and operation of a non-metallic pilot CO₂ capture rig and the influence of iron

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Executive summary

This deliverable summarizes the efforts towards the construction and operation of a non-metallic pilot CO_2 capture rig, performed within the LAUNCH project, to generate further understanding of amine solvent degradation. The full deliverable (paper and presentation) was presented at the GHGT-16 conference in Lyon, France. A more elaborate summary of the results can be found in the paper below.

Construction and Operation of a non-Metallic Pilot CO2 Capture Rig

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Abstract

This study describes the construction and operation of a non-metallic pilot CO2 capture rig, built in the LAUNCH CCUS project to analyse oxidative solvent degradation in a continuous CO2 capture process where metal concentrations in the solvent are constant. This can aid in creating better understanding of oxidative degradation of amine solvents, and can further help to evaluate the potential of building non-metallic CO2 capture systems. The equipment and material selection for the non-metallic rig is discussed. A first campaign is conducted using MEA as the capture solvent, where the iron concentration in the solvent is gradually increased over the course of several weeks. In the start of the campaign, the rig could be operated according to its design specifications. This was not possible anymore in the final part of the campaign, due to leakages occurring at the stripper, and water balance issues. Liquid phase analysis of the solvent during the campaign shows the concentration of MEA, concentration of metals and concentration of major oxidative degradation products. Results from the analysis in this campaign should be analysed with caution, since the operation of the rig was not stable in the latter part of the experiment. The results from the experimental campaign give a first indication of the usefulness of operating such a non-metallic CO2 capture rig to give further insights in oxidative degradation, while also giving insights where difficulties are in designing CO2 capture systems without metal equipment. For a potential future campaign, the rig should be redesigned to fix some of the problems encountered in this first campaign, and it is recommended that in a next campaign, the rig is operated for several months without adding any metals to the solvent.

Keywords: CO2 capture; non-metallic capture rig; oxidative solvent degradation; solvent stability;

1. Introduction

Solvent degradation poses considerable challenges to post combustion capture processes using amines [1]. In longer test campaigns running with MEA, a sudden increase of degradation products and dissolved metals in the solvent are reported [2]. In full-scale operation, this could lead to high operational costs and solvent management strategies are necessary to control the degradation of the solvent. The exact mechanism for this degradation is currently still not fully understood and it is therefore hard to predict and control solvent degradation. Therefore, in the past years, a lot of research in post-combustion capture is devoted to these solvent degradation mechanisms, both from a fundamental and practical perspective. In the LAUNCH CCUS project (https://launchccus.eu), universities, knowledge institutes and industry work together to gain a better fundamental understanding of solvent degradation and further develop solvent management strategies.

One of the activities to gain a better fundamental understanding of solvent degradation is the operation of a pilot CO2 capture rig, that is fully constructed out of non-metallic equipment (at least for the parts that are in contact with the solvent). Cyclic operation in this regard is important, since in this way it is possible to obtain similar degradation behaviour as observed in (pilot) capture plants [3]. As compared to prior bench-scale rigs, built in stainless steel, this non-metallic rig can give a better understanding of solvent degradation under cyclic operation with constant metal concentrations, as the solvent cannot uptake any metals from the capture rig. This paper describes the construction of the rig and the results of the first campaign operated with this rig.

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2. Design and construction

The non-metallic capture rig is designed by TNO, BEFORM and Goodtech AS. The rig is based on a standard CO_2 capture process with an absorber and desorber section, and the final process and instrumentation diagram for the rig is shown in Figure 1.

The columns are designed to handle a maximum flue gas flow of 4 Nm^3/hr, resulting in an internal diameter of ca. 4 cm. The packing heights used in the absorber and desorber are 1.2 meter divided over two sections per column. The column material is a special formulation of BEFORM, based on results of the FANGST project (Norwegian national project). It consists of a carbon fiber epoxy, coated with a gelcoated epoxy innerliner, as shown in Figure 2. The packing material used in the first test campaign is ceramic random packing. On the absorber side, there is a condenser section at the top of the column, where indirect cooling with cooling water is performed through flexible tubes that run throughout this column. The sumps of the columns are designed to give a solvent inventory of ca. 20 liters. There are multiple temperature sensors (Endress+Hauser) in the absorber and desorber, which are placed externally on the surface of the columns. In the absorber sump, there is a level measurement, based on pressure differential between the inlet gas and the pressure at the bottom of the sump. These pressure sensors are membrane type pressure sensors (Stork Solutions), and therefore circumvent any contact between the metal and the **solvent**. A similar control is used in the desorber, where the pressure in the bottom of the sump is measured, and is compared with the measurement in the top of the stripper, to determine the level in the stripper. The reboiler used in the non-metallic plant is a thermosiphon reboiler (WOOAM SUPER POLYMER CO.,LTD). This is a metal shell and tube heat exchanger with PTFE lines running through the heat exchanger. This means that on the tube side, where the solvent is heated, no contact between metal and solvent occurs. On the shell-side, an external hot-oil loop is used, that is not in further contact with the process (this hot-oil loop is in contact with metal). The other heat exchangers in the rig are PFA shell and tube heat exchangers (ElringKlinger).

The pumps used in the set-up are peristaltic pumps (Watson-Marlow), again to circumvent solvent exposure to any metals. Additionally, pulse dampeners (White Knight) are installed to limit the pulsing effect expected from peristaltic pumps.

Lastly, on the top of the stripper, a pressure relieve valve is placed (Badger Meter). This valve is placed in the gaseous CO_2 product line (after water condensation) so that under normal operation, no solvent exposure to this pressure control valve can occur. Therefore, it is possible to have a metal based equipment for this.

The resulting plant, as manufactured by Goodtech AS and BEFORM, and installed at TNO, can be found in Figure 3. All tubing and connections used in the plant are based on PTFE/PFA type of plastics, because of their expected compatibility with amines and durability under the required process conditions.
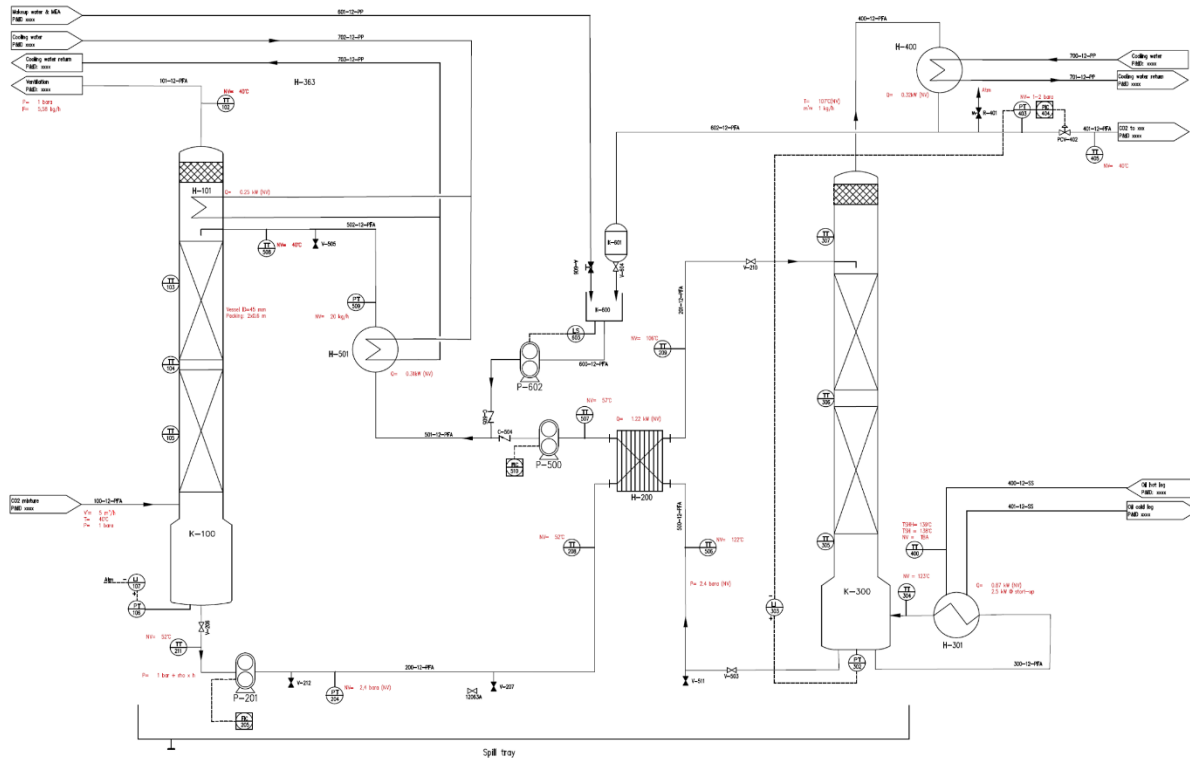

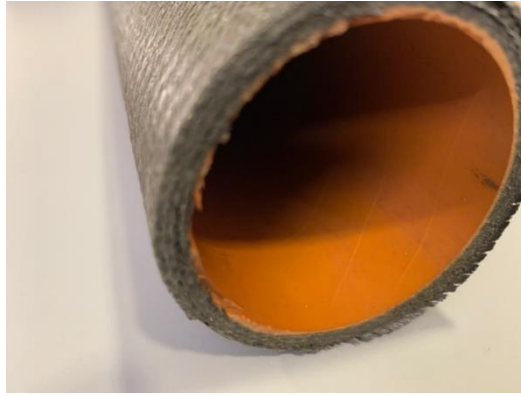Figure 1, process and instrumentation diagram for the non-metallic capture rig.

Figure 2, Cross section of absorber and desorber
material used in the non-metallic capture rig.

Figure 3, Picture of the non-metallic capture rig, as installed at TNO.

3. Experimental plan

In the first campaign of the non-metallic capture rig, mono-ethanolamine (MEA) is used as the solvent, as MEA is often used as a benchmark solvent and a lot of knowledge is build up on this solvent in the past decades. Additionally, MEA is a relatively fast degrading solvent, which makes it a suitable solvent to use in relatively short lab-based campaigns, as any degradation will be visible earlier than for most other solvents.

During the campaign, iron is dosed (iron(II) sulfate) on a weekly basis, increasing the metal concentration periodically. That means that during a week, the metal concentration should not change, because no additional metals can be taken up by the solvent. The first week of experiments are performed with fresh MEA, without any metals added to the solvent, and gradually metals are added according to the plan shown in Table *1*. Iron is chosen as the only metal to be added in this first campaign, as iron is often present in the solvent due to corrosion of the equipment, and is often one of the main metal correlated with solvent degradation in literature [2].

Table 1, plan for iron dosing during the campaign

Week	Iron concentration in solvent (mg/kg)
1	0
2	1
3	5
4	10
5	50
6	100

For the campaign, synthetic flue gas is used, consisting of air, mixed with pure CO_2 (99.7% purity). A CO_2 concentration of ca. 20-25 vol% is used throughout the campaign at a total flow rate of 3.3 Nm^3/hr. The main reason for using this high CO_2 concentration is to increase the mass transfer in the absorber, since there is only 1.2 meters of packing height available. Additionally, a quench is installed upstream of the absorber column, to saturate the synthetic flue gas with water, so the water balance can be satisfied in the rig, and to pre-heat the flue gas to the desired absorber temperature (40 ℃).

During the campaign, the process inputs are kept as stable as possible. The stripper pressure is controlled at 0.85 barg by the pressure control valve, the lean solvent flow is fixed at 25 L/hr, and the rich solvent flow is controlled by the absorber level.

4. Results

4.1. Overview of first campaign and stability of operation

The campaign was originally planned to start in March 2022, although during commissioning, it was found that several adjustments were needed to the rig to run a successful campaign. Modifications were mainly needed on the (flanged) connections of the stripper.

The actual campaign with MEA was started on the 14th of July 2022. The campaign has lasted a total of 12 weeks, with periods where the process was not operational. Figure 4 shows the top stripper pressure during the complete campaign. This parameter is especially relevant for determining when the system was operating at the desired (and controlled) operating pressure of 0.85 barg.

It can be seen that the dosing of metals did not occur every week, due to the non-stable operation of the process. It was therefore decided to only add the metals after a week of successful operation (defined by stripping CO_2 from the process), and has resulted in the addition of metals according to the times shown in Figure 4. This reasoning was only used for the addition of the first three batches of iron(II) sulfate. During the last weeks of the operation, the process was not steady (explained further below) and the metals were added earlier than after a week of successful operation. Additionally, there is almost a month in the middle of the campaign, where the oil-bath (that heats the process) was not functioning properly, which further delayed the testing.

At the start of the campaign, there were almost no leakages in the plant, and the pressure in the stripper could be maintained at 0.85 barg. Throughout the campaign, more and more solvent started to leak from the stripper. While initially, small leakages occurred at the connections to and from the reboiler and around the flanges of the stripper, eventually also the column itself started to leak in various places, as shown in Figure 5. During the campaign, fresh solvent was added regularly to maintain the desired solvent inventory in the process.

Because of these leakages, it became harder to maintain the stripper pressure. From Figure 4, it can be seen that the operating pressure of 0.85 barg could not be maintained anymore in the stripper, and the set-point was decreased to 0.65 barg, which was the operating value for the final weeks of the campaign.
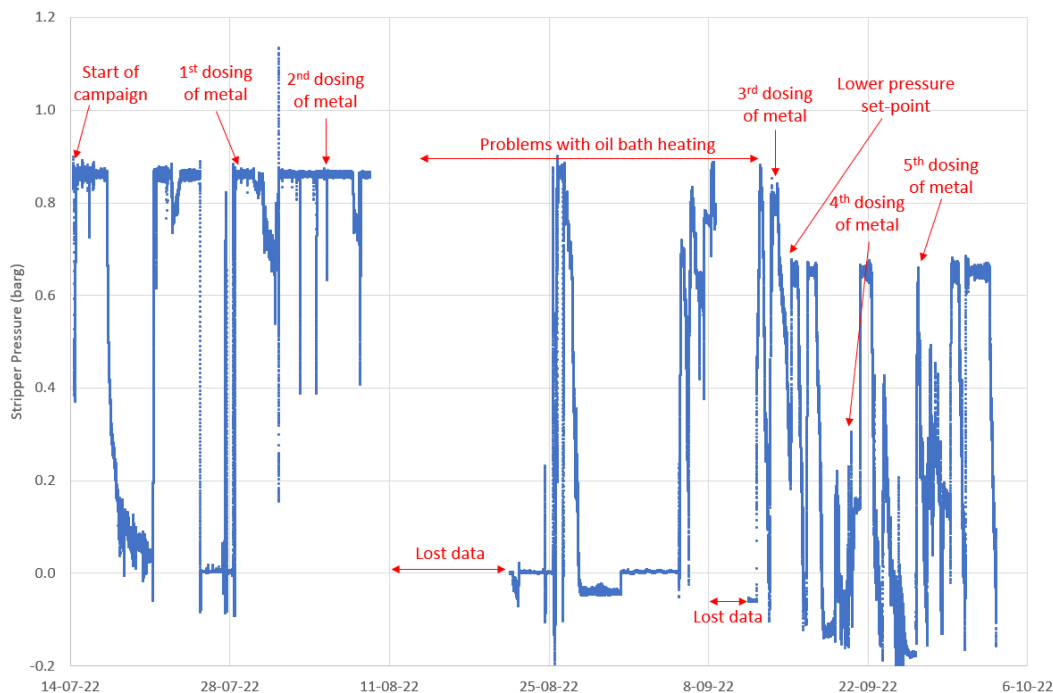
Figure 4, overview of stripper pressure throughout the campaign, including main events.

Figure 5, leakages in the non-metallic capture rig, both in the stripper column and connections to the reboiler.

4.2. Liquid phase analysis

During the campaign, liquid samples were taken regularly for analysis of the liquid phase. The liquid phase has been analysed for MEA concentration (by ion-chromatography), major oxidative degradation products (by ion-chromatography) and metals (by inductively coupled plasma mass spectrometry). No samples were taken during the longer stop in the middle of the campaign.

The MEA concentration in the solvent during the campaign is shown in Figure 6. The MEA concentration in the start of the campaign was relatively well controlled between 20-30 wt%. During the final part of the campaign, the control of the MEA concentration became worse, because of the unstable operation caused by the leakages and water balance problems in the capture rig. MEA concentrations of up to 60% were measured, which are concentrations far outside the normal operational window. In the last sample of the campaign, the MEA concentration has been reduced to normal operating conditions again by adding mainly water to the rig. The water balance in the rig is mainly dependent on the quench performance (upstream of the absorber) and the efficiency of water condensation in the top of the absorber. In this campaign, the quench regularly stopped, decreasing the amount of water coming into the rig, disturbing the water balance and increasing the solvent concentration. Additionally, there is no classical water wash section in the rig, but rather an internal cooling section, with indirect water cooling, where the water and amines can condense and return to the absorber. The efficiency of this method of condensation is not known for this rig, and it is recommended that in a future campaign, either a full water wash is installed, or the gas is cooled outside of the column and condensed water with solvent is returned (with a pump) to the absorber.

The solvent has been analysed for chromium, iron, nickel and copper. The metal concentrations throughout the campaign can be seen in Figure 7. In the fresh MEA, no metals could be detected. The detection limits for chromium, iron, nickel and copper are 0.02, 0.08, 0.02 and 0.1 mg/kg respectively for the analysis used. After two weeks of testing, all metals are detected, but all under

1 mg/kg. The origin of these metals is unknown, but it might be possible that there were still trace amount of solvent from the commissioning campaign in the rig (although the rig was cleaned multiple times with water). The different dosing times of the iron sulfate are indicated in Figure 7, and it can be seen that the experimental plan from Table *1* was relatively well followed. The other metals analysed for stay relatively constant throughout the campaign, and for copper and chromium specifically, the concentration drops below the measurement limit for the final part of the campaign. For the last sample shown in the graph, the dilution effect of water addition can be observed, as the iron concentration drops from 92 to 15 mg/kg.

The concentration of major oxidative degradation products can be found in Figure 8. For this campaign, formic acid, acetic acid and oxalic acid are analysed as major oxidative degradation products. For the fresh MEA sample, very low concentrations of degradation products are observed. It can be seen that formate is the most prevalent degradation compound in this campaign in the beginning of the campaign. The concentration of these degradation products seems to increase relatively constant during the first part of the campaign with iron concentrations up to 5 mg/kg. The latter part of the campaign is hard to analyse, because of the unstable operation of the plant, resulting in varying MEA concentrations and an unstable water balance, which also varied the concentration of the degradation products heavily. The last sample in the campaign seems to show exponential degradation, as the concentration of all degradation products are increased steeply, while the solvent is diluted heavily, as shown by the concentration of MEA and metals in Figure 6 and Figure 7.
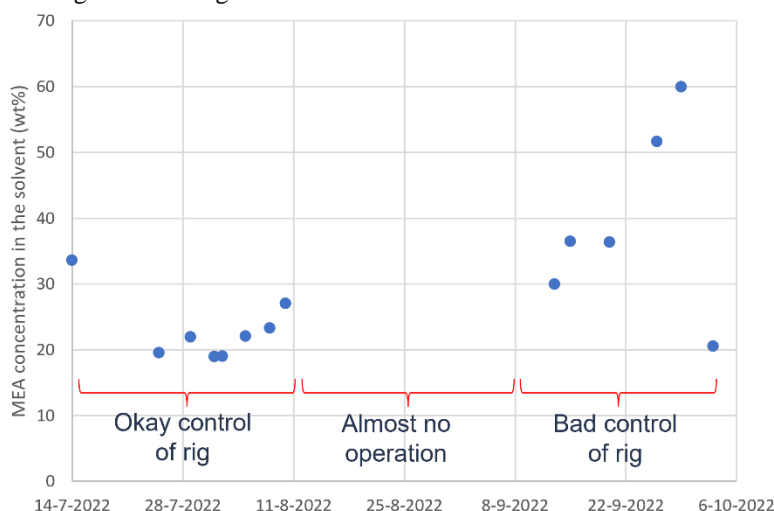

Figure 6, MEA concentration in the solvent during the campaign.
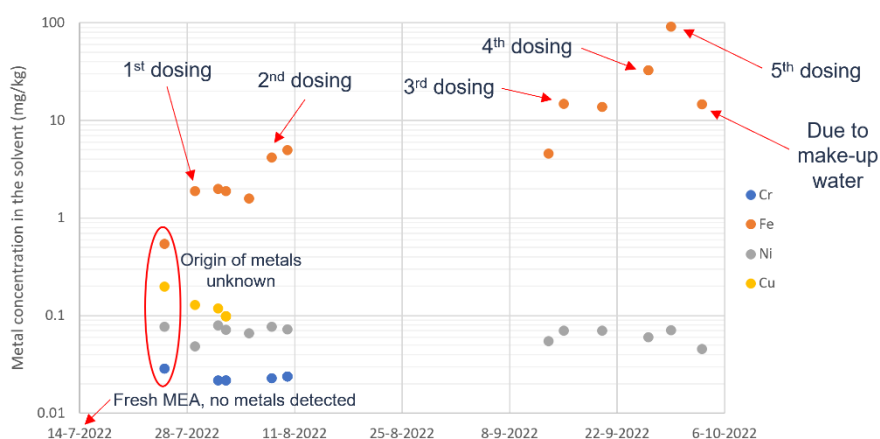

Figure 7, concentration of iron, chromium, nickel and copper in the solvent during the campaign.
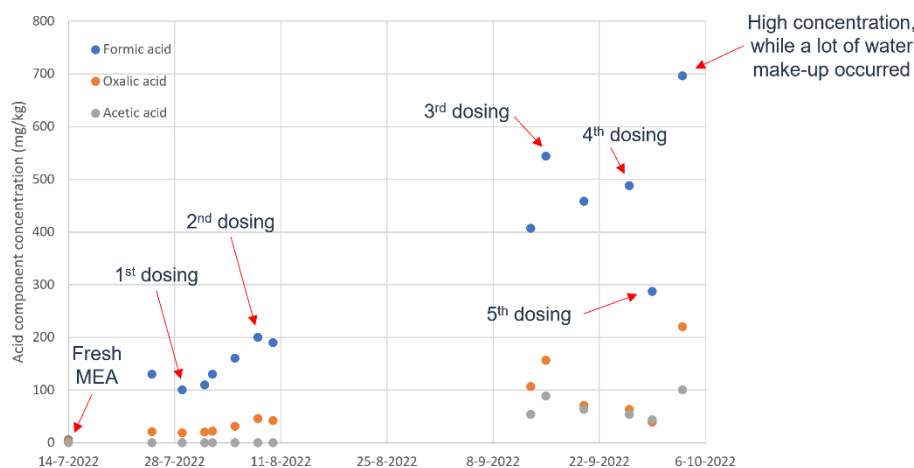
Figure 8, concentration of major oxidative degradation products of MEA
in the solvent during the campaign.

5. Conclusions and recommendations

In this study, a non-metallic capture rig was built for cyclic testing of CO_2 capture solvents under conditions where the solvent does not touch any metal equipment, and the metal concentrations can be controlled in the solvent.

The first campaign with MEA has shown that the non-metallic capture rig can operate under steady cyclic conditions where CO_2 is stripped at 0.85 barg from the solvent, similar to normal metal-based CO_2 capture processes. Liquid analysis on the metal concentration in the solvent has further shown that the iron concentration in the solvent remains constant between dosing periods of the metal, which further shows the potential of running a non-metallic CO_2 capture rig to further the understanding of solvent degradation in amine solvents.

However, in this first-of-a-kind capture rig, many problems have occurred (during the latter part of the campaign) with leakages in the stripper (connections and column itself) and the water balance of the plant. Therefore, the result shown in this paper should be mostly seen as a first indication of how such a non-metallic rig could help us further the understanding of solvent degradation under controlled metal concentrations and should also give indications where current difficulties are in designing a fully non-metal CO_2 capture plant.

For a potential future campaign, it is recommended to redesign of the non-metallic capture rig where: (1) the absorber and desorber columns are replaced by using a more suitable and durable material, (2) the quench and water wash are redesigned and integrated with the non-metallic capture rig, (3) more packing height should be installed in the absorber to allow for better mass transfer rates to the liquid phase, and to better represent commercial processes, (4) an online solvent concentration measurement device is installed to better control the solvent concentration (and water balance) of the rig. A future campaign should focus on the long-term stability of the solvent under cyclic operation without adding any metals to the system, in a campaign lasting at least several months. This could generate further insights in oxidative degradation (rates) of amine solvents under conditions with very little metals in the solvent, and could additionally help further assess the potential benefits of creating (partially) non-metallic CO_2 capture processes.

References

[1]   V. Buvik, K. K. Høisæter, S. J. Vevelstad, and H. K. Knuutila, "A review of degradation and emissions in post-combustion CO2 capture pilot plants," *Int. J. Greenh. Gas Control*, vol. 106, 2021, doi: 10.1016/j.ijggc.2020.103246.

[2]   P. Moser *et al.*, "Results of the 18-month test with MEA at the post-combustion capture pilot plant at Niederaussem – new impetus to solvent management, emissions and dynamic behaviour," *Int. J. Greenh. Gas Control*, vol. 95, p. 102945, Apr. 2020, doi: 10.1016/j.ijggc.2019.102945.

[3]   S. J. Vevelstad *et al.*, "Comparison of different Solvents from the Solvent Degradation Rig with Real Samples," *Energy Procedia*, vol. 114, pp. 2061–2077, 2017, doi: 10.1016/j.egypro.2017.03.1341.

Acknowledgements

Construction and operation of a non-metallic CO$_2$ capture rig

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Introduction – Solvent degradation

- Solvent degradation poses significant challenges to post-combustion capture systems

- Metals are part of the problem, and are thought to catalyse the degradation of the amine

- The exact mechanisms is not fully understood

- This makes it hard to predict and control solvent degradation (for commercial processes)
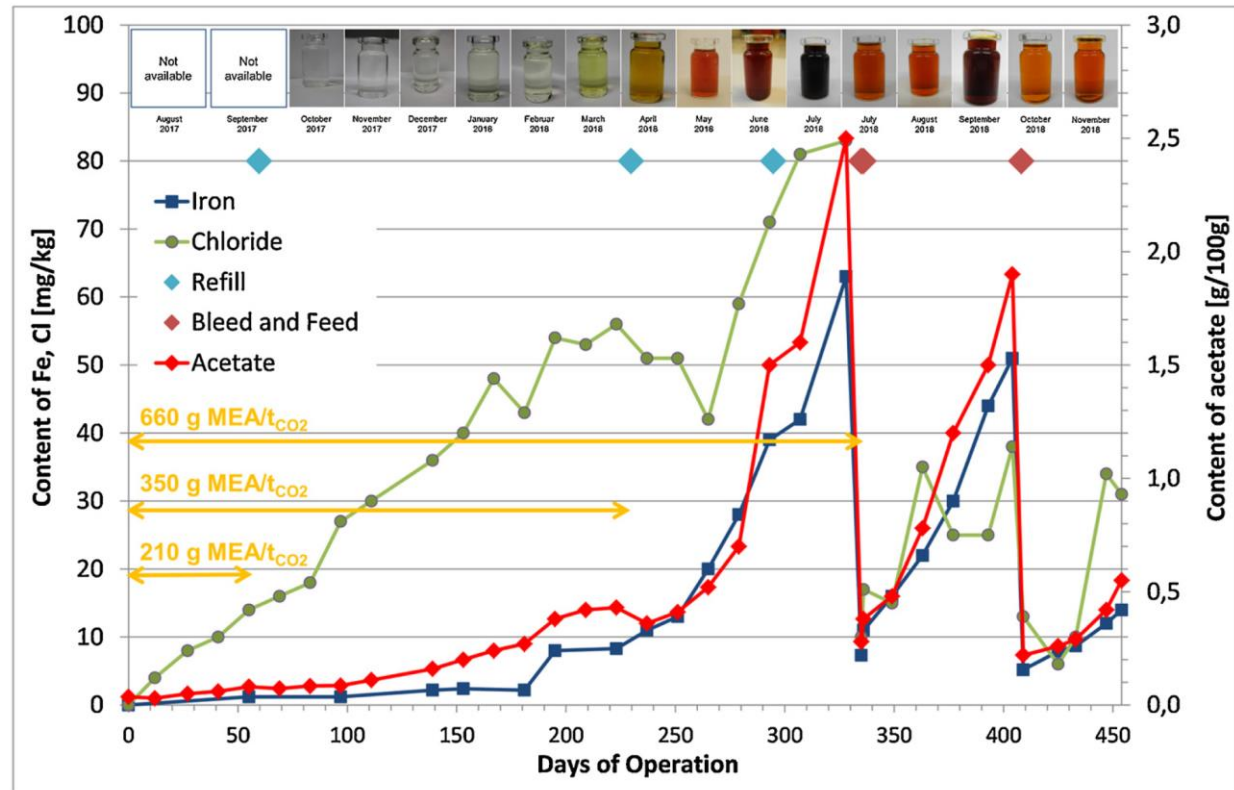
Introduction – LAUNCH CCUS project
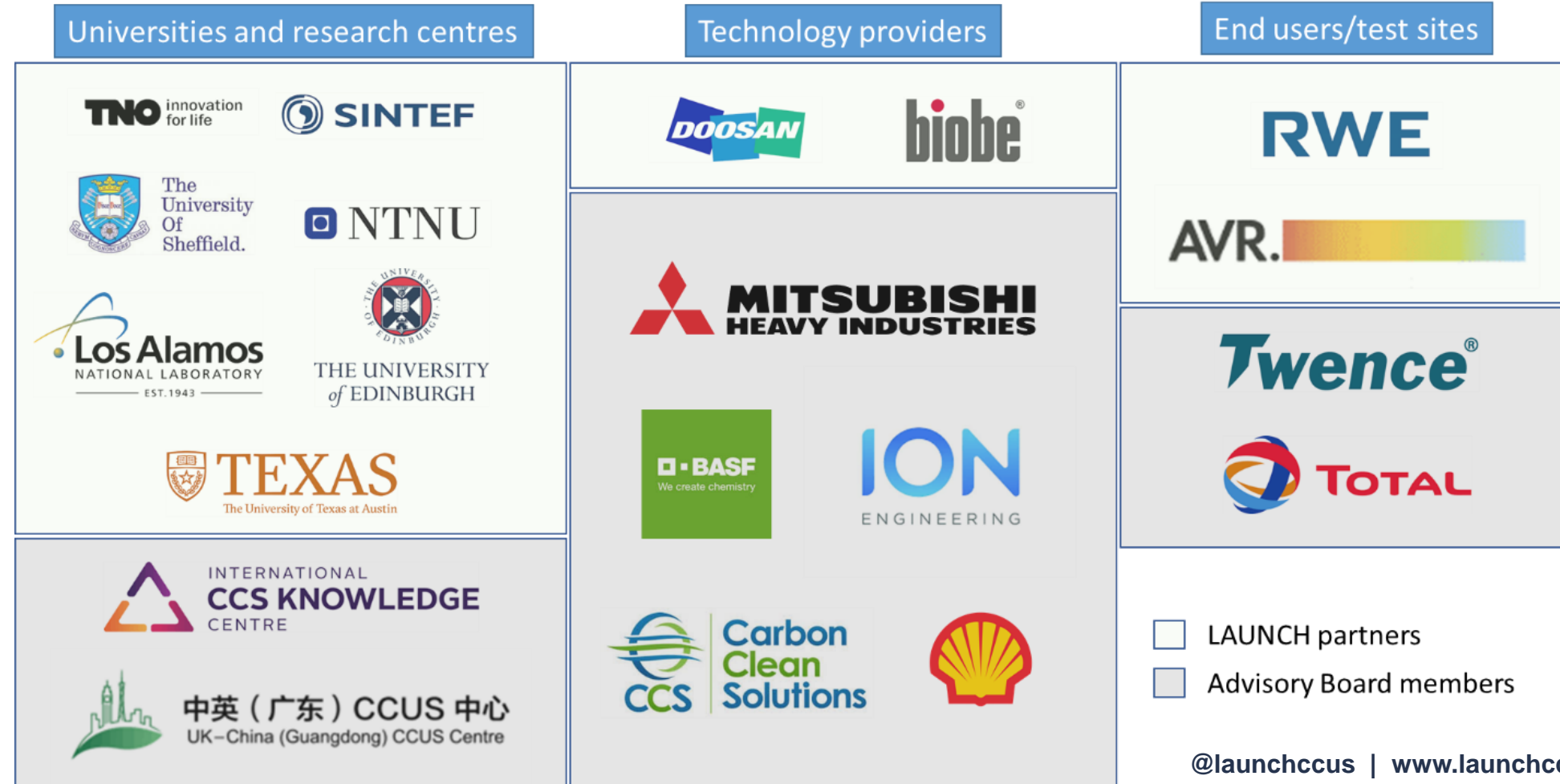
Introduction – LAUNCH CCUS project

Design and construction of non-metallic rig

TNO   **BEFORM**   **Goodtech**
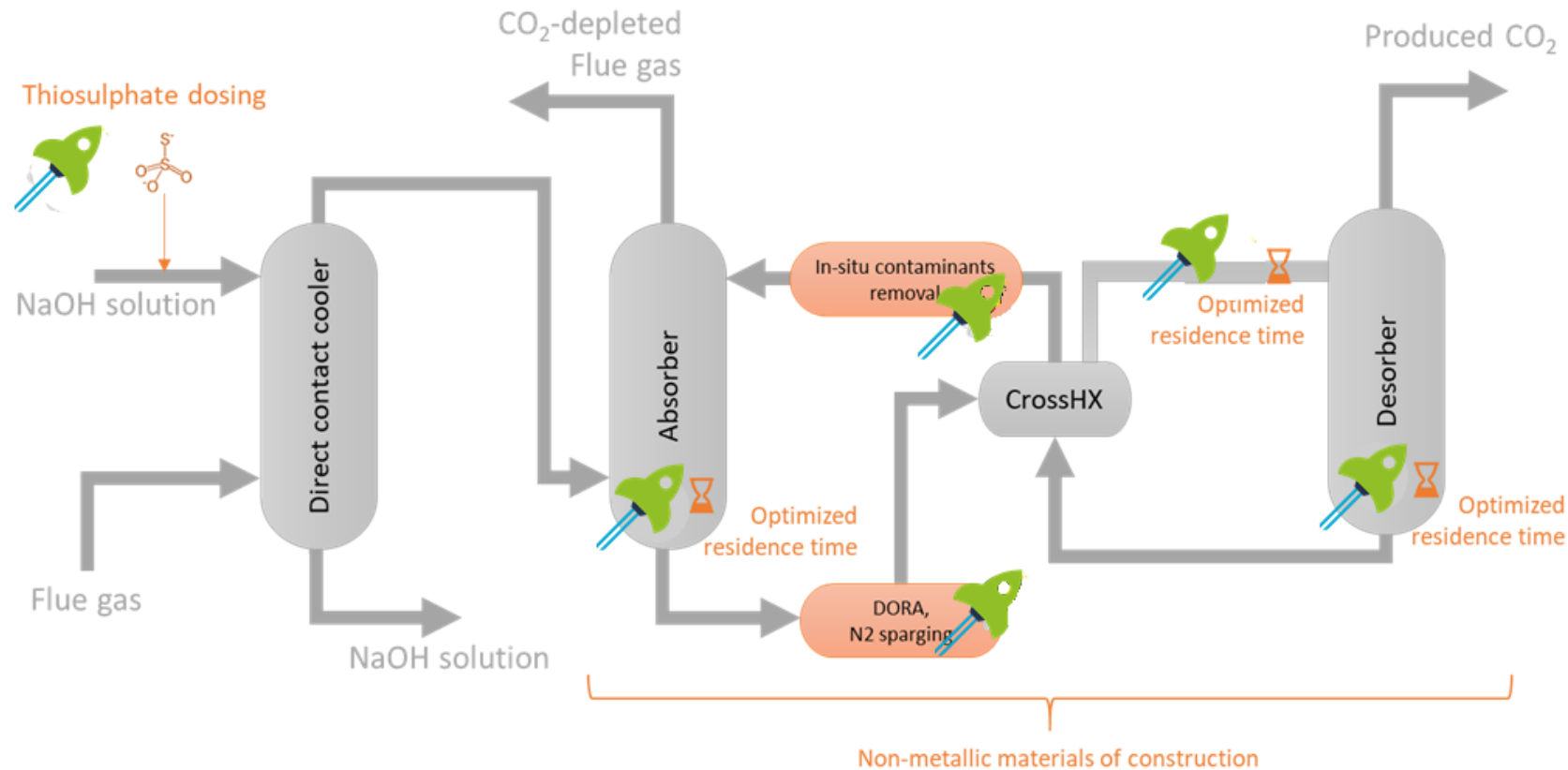
Goal: Build and operate a CO_2 capture rig, where the solvent does not touch any metal equipment

Three companies have combined resources to create the non-metallic rig:

- TNO → Dutch research institute with expertise on CO_2 capture systems

- BEFORM (previously Biobe) → Norwegian company, experts in plastic materials

- Goodtech → Norwegian company, engineering services & supplier

Design and construction of non-metallic rig

Process & Instrumentation Diagram
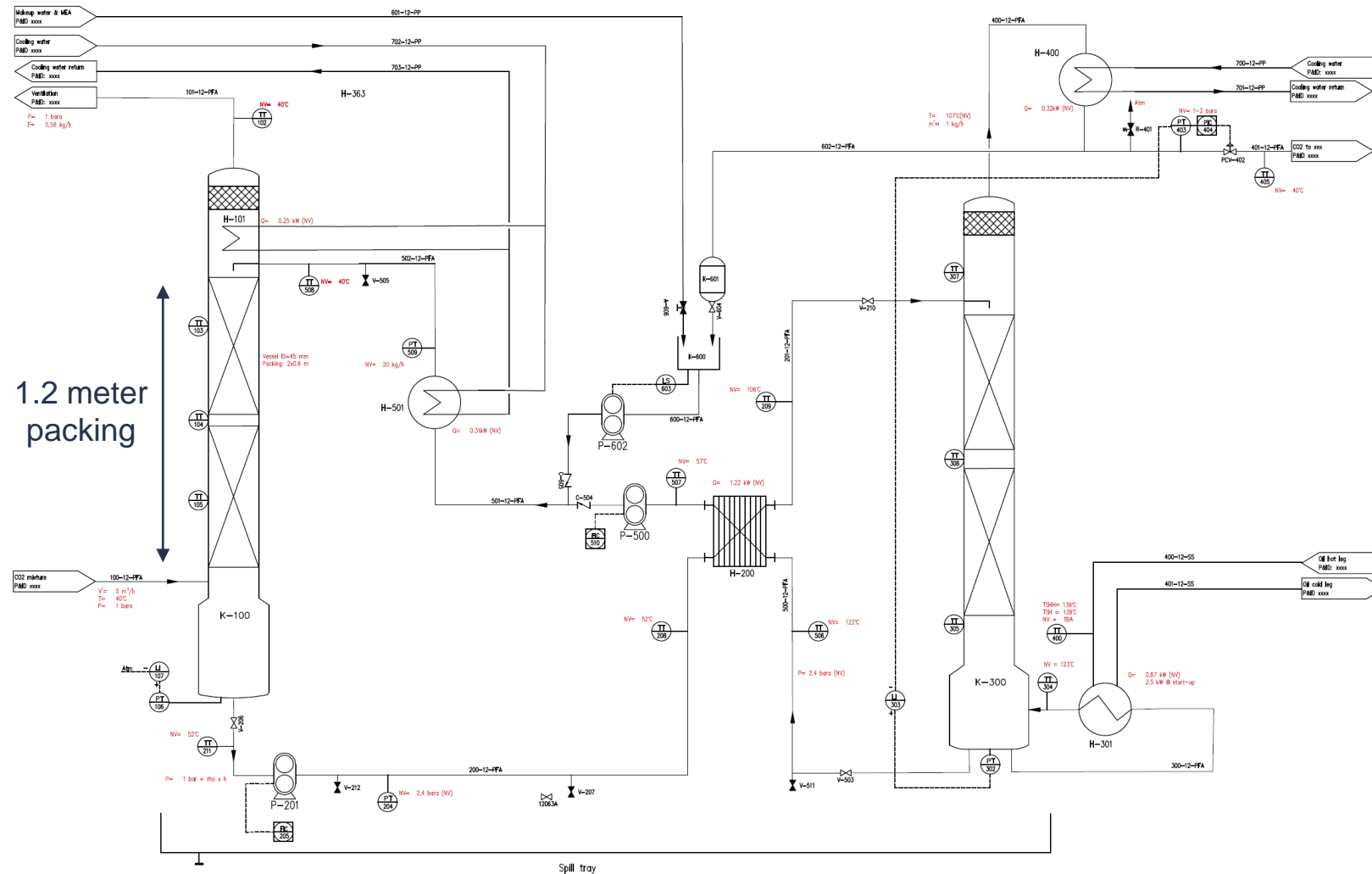
Design and construction of non-metallic rig

Main equipment

Columns: carbon fiber epoxy tubes, coated with a gelcoated epoxy innerliner, created by BEFORM
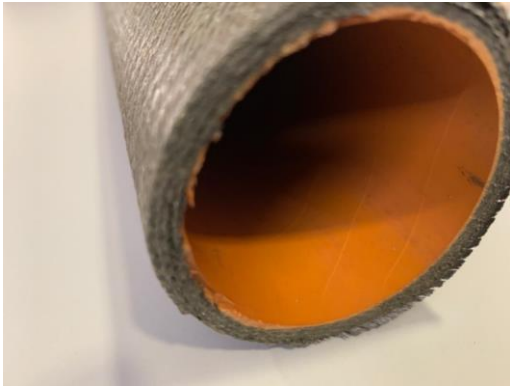
Reboiler: PTFE tubed shell and tube heat exchanger from WOOAM Super Polymer

Heat exchangers: PFA shell and tube heat exchangers from ElringKlinger

Pumps: Peristaltic pumps from Watson-Marlow

Picture source: http://eng.wooamsp.co.kr/

Picture source: https://www.elringklinger-engineered-plastics.com/products/thermo-xtm-shell-and-tube-heat-exchanger/

Picture source: https://www.wmfts.com/en/watson-marlow-pumps/cased-pumps/500-series-cased-pump/

Design and construction of non-metallic rig
Sensors and control

➢ Temperature sensors: PT 100 sensors, on the outside of the columns and tubing

➢ Pressure differential measurement above and below liquid level in absorber/desorber to calculate liquid level
  - Metal: In feed gas
  - Non-metal: Below sumps and stripper top

➢ Liquid flow: Calculated from speed of peristaltic pump

➢ Pulse dampeners: To lower the pulsing coming from the peristaltic pumps

➢ Pressure relieve valve on top of stripper: To control pressure (metal)

➢ Tubing/valves/connections: PTFE or PFA equipment

The final product

Experimental plan for first campaign

In a first campaign, iron will be added gradually over the course of 6 weeks. Synthetic flue gas is used in the campaign. The solvent used is 30 wt% MEA.

Week (-)	Iron (II) concentration in the solvent (mg/kg)
1	0
2	1
3	5
4	10
5	50
6	100

Overview of the first campaign

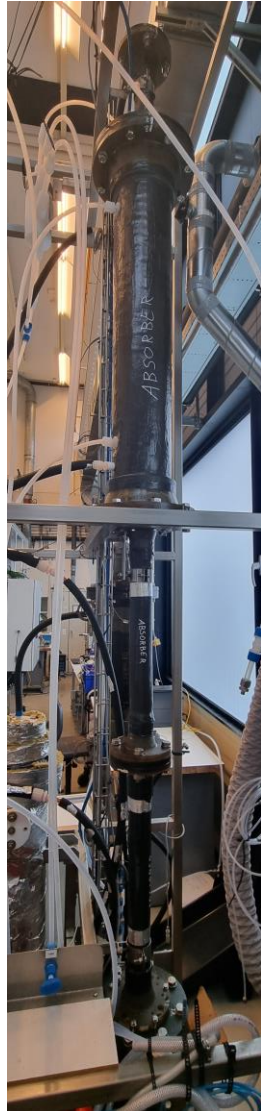The stripper pressure is shown as an indicator of the performance of the rig.
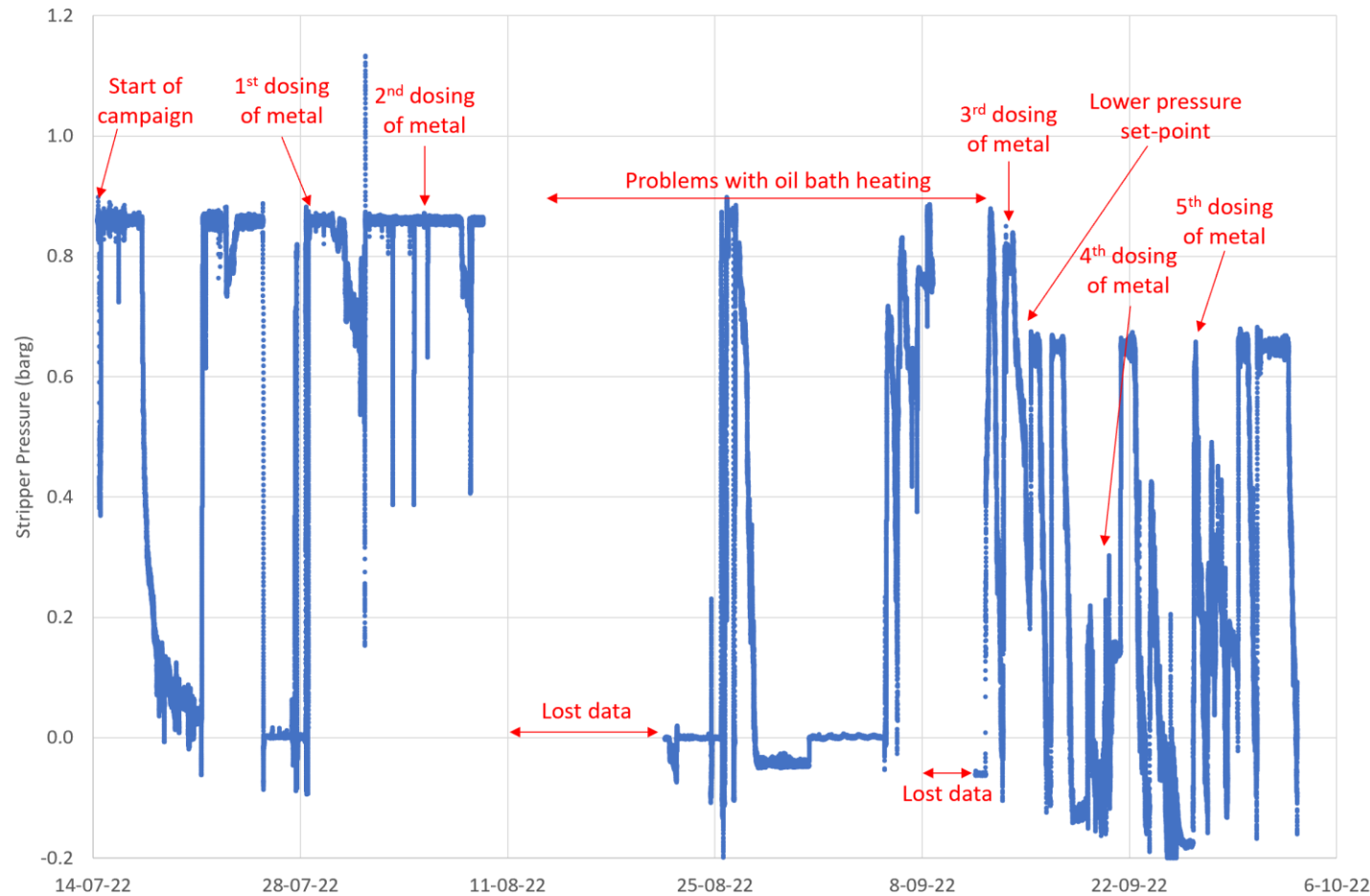
Leakages in the plant

During the campaign, leaks were observed in the stripper column and connections in the stripper (sump), which became worse over time.
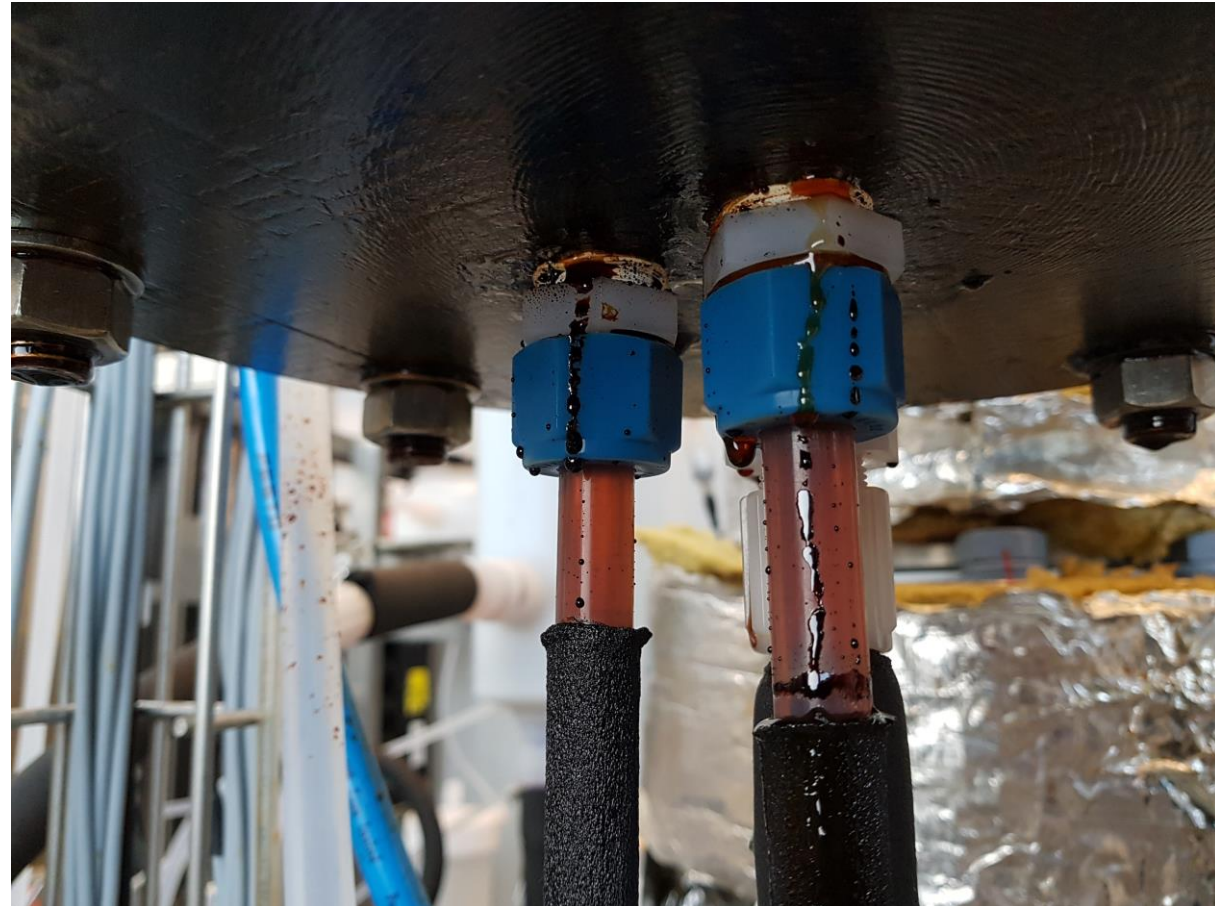
Water balance problems

Absorber wash: Wider column equipped with flexible heat exchanger lines to cool the flue gas back to inlet temperatures

Picture source: https://ph.parker.com/us/en/high-purity-pfa-heat-exchanger-hpx1-series

Quench (metal): To pre-heat the flue gas and saturate the flue gas with water

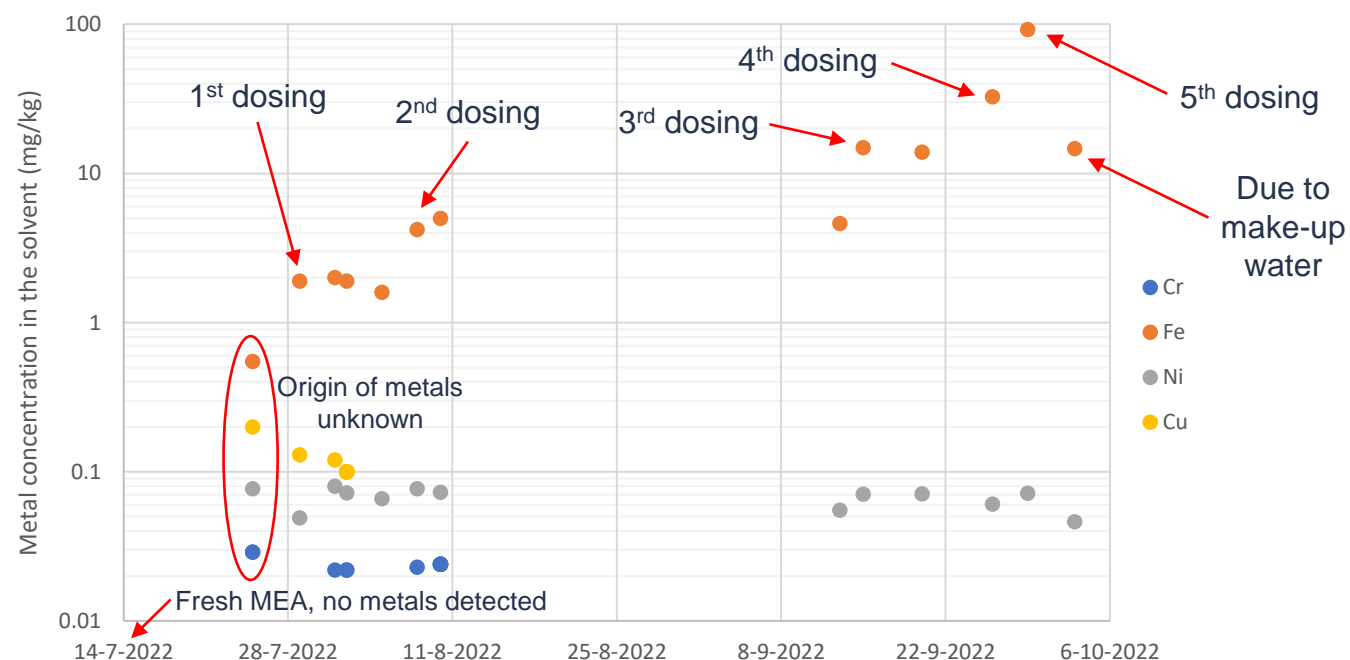For potential future campaigns, both quench and water wash must be fully redesigned
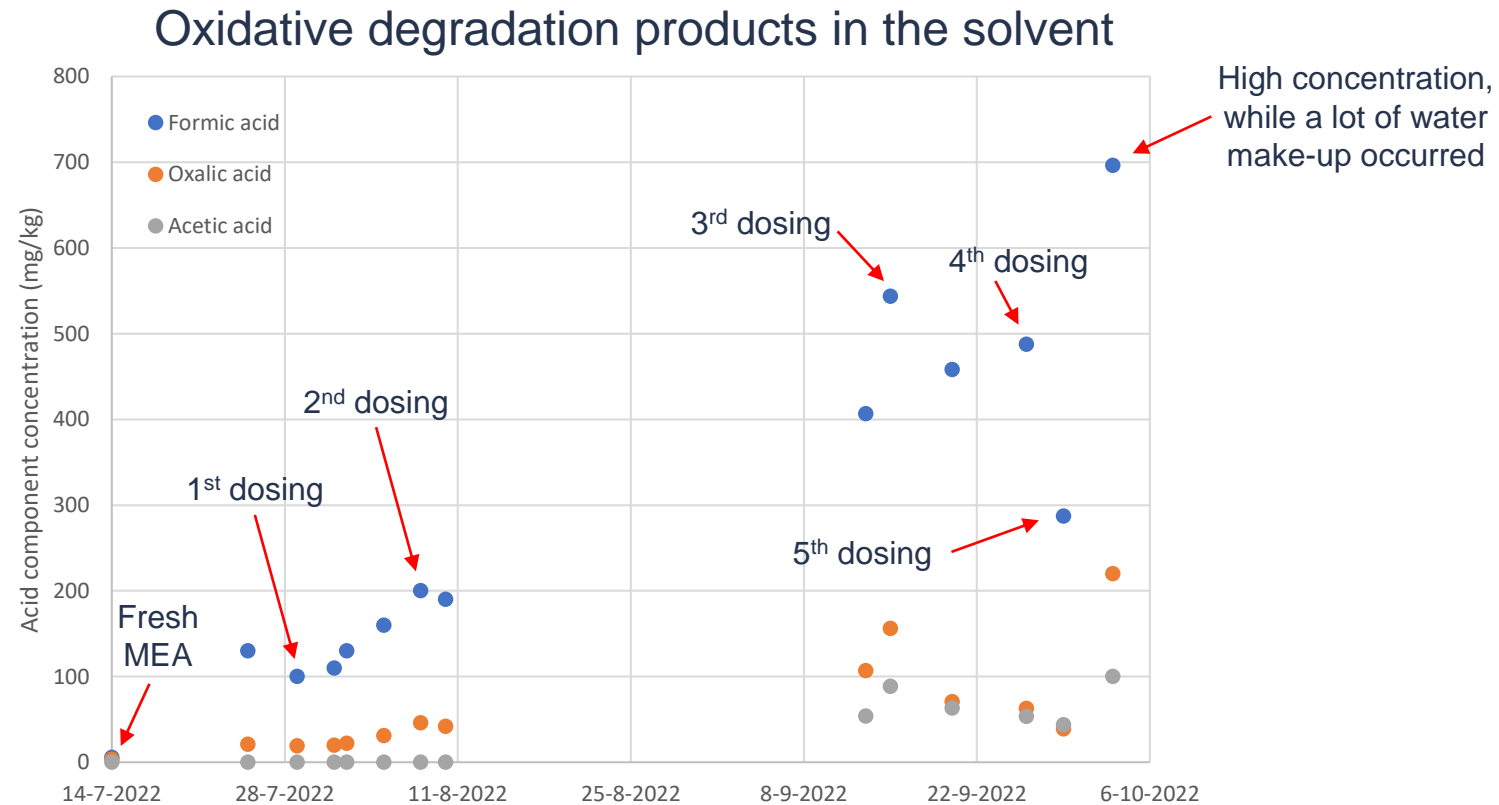
Results

The MEA concentration in the solvent
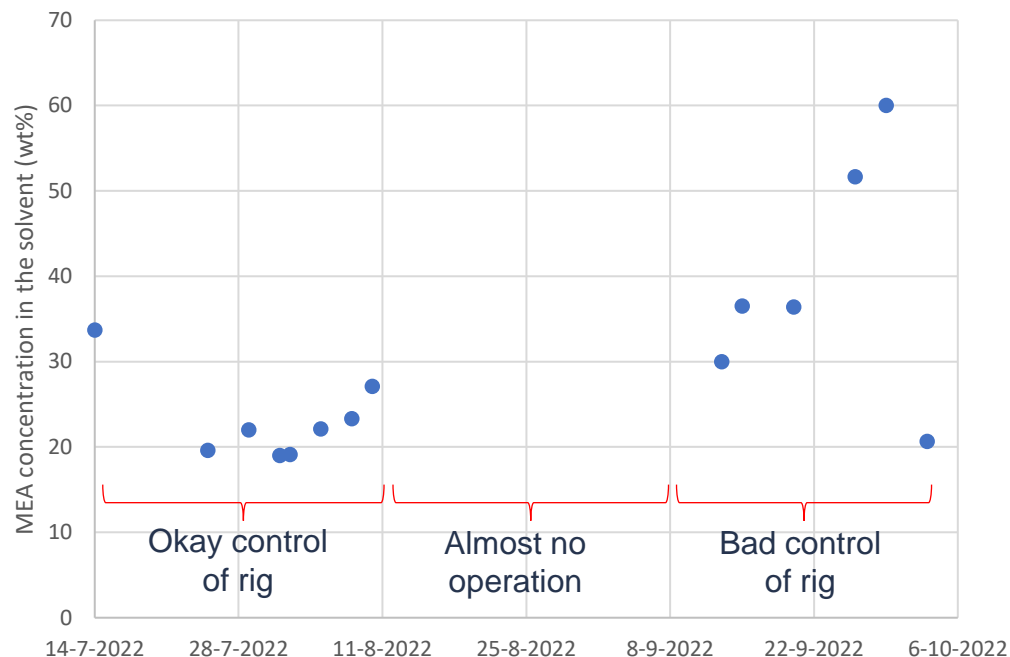
The MEA concentration was relatively well controlled in the start of campaign, but could not be well controlled near the end of the campaign

The metal concentration in the solvent

The iron dosing during the campaign was successful, and levels up to 100 mg/kg were reached. Other metals are only present in very low numbers (near or below detection limit).

Results

Oxidative degradation products in the solvent

- Formic acid
- Oxalic acid
- Acetic acid

Fresh MEA

1st dosing

2nd dosing

3rd dosing

4th dosing

5th dosing

High concentration, while a lot of water make-up occurred

Acid component concentration (mg/kg)

14-7-2022   28-7-2022   11-8-2022   25-8-2022   8-9-2022   22-9-2022   6-10-2022

Observations:
- Degradation products increase even with very little metals present in the solvent
- With 100 mg/kg metals, oxidative degradation seems accelerate very quickly
- Degradation product formation is similar to commercial systems (formate>oxalate>acetate)

Conclusions

➢ A non-metallic CO_2 capture rig was successfully build in the LAUNCH project

➢ A first campaign is conducted, where iron is gradually dosed in the solvent

➢ Quite some problems occurred during operation: leakages, water balance problems, MEA losses

➢ The iron dosing was successful, and the iron concentration seems to remain constant between periods of dosing the metals. Other metals are present in very low concentrations or are not detected

➢ Degradation already occurs with very little metals in the solvent. With high iron concentrations near 100 mg/kg, the degradation seems to accelerate quickly

➢ Degradation product formation is similar to commercial systems (formate>oxalate>acetate)

Recommendations

➢ For a future campaign with the non-metallic rig, the absorber and desorber need to be completely redesigned, so that no leakages occur during the (long-term) campaigns

➢ The quench and water wash need to be redesigned to satisfy the water balance in the process

➢ More packing height is recommended, as 1.2 meter gives little mass transfer to the liquid phase, which makes it harder to compare the results with other processes

➢ Online solvent measurements would help further control the MEA concentration in the rig

➢ A long campaign (ca. 6 months) without adding any metals could give further insights in the long-term degradation behaviour without increased concentrations of metals in the solvent → This also gives further insights in potential benefits of using non-metallic equipment for CO_2 capture.

Acknowledgements

Questions?