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## Impact of dissolved oxygen removal on solvent degradation for post-combustion CO<sub>2</sub> capture

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### ABSTRACT

One of the major issues encountered in the Post Combustion CO<sub>2</sub> Capture processes is the degradation of the solvent which can be in great part attributed to the presence of oxygen in the solution. The present report focuses on the demonstration of DORA (Dissolved Oxygen Removal Apparatus), a technology developed by TNO as a counter-measure of oxidative degradation. The DORA was first operated in combination with TNO's mobile bench-scale CO<sub>2</sub> capture pilot (5 Nm<sup>3</sup>/h flue gas capacity) with artificial flue gas, showing an instant drop of 15% and an overall reduction of approximately 70% in the ammonia emissions from the absorber, which is an indication of reduced degradation. The technology was also demonstrated using the same pilot in an industrial environment in collaboration with the facility PlantOne bringing DORA from TRL5 to TRL6. This campaign proved that DORA contributed to the deceleration of solvent degradation. The tests were executed with a porous membrane, and it was observed that exposure to degraded solvents led to solvent leakage through this membrane. Therefore, the use of a coated membrane was proposed to optimize the operation and increase oxygen removal. The use of this membrane is demonstrated at TRL3. Along with that, a model was developed to determine mass transfer resistances and the membrane area required to remove different levels of dissolved oxygen.

### Keywords:

PCCC; Oxidative degradation; Solvent management; Membrane; Removal of dissolved oxygen

### Nomenclature

MEA Monoethanolamine

DORA Dissolved Oxygen Removal Apparatus

TRL Technology Readiness Level

L-L Liquid-liquid membrane operation mode

L-G Liquid-gas membrane operation mode

## 1. Introduction

One of the major challenges of post-combustion CO<sub>2</sub> capture is the degradation of the solvent during operation which can lead to a significant increase in costs through solvent losses, corrosion of equipment, higher emissions and complexity in solvent handling. These issues are a consequence of the formation of degradation products, which include volatile products (such as ammonia) and heat stable salts (such as formate, acetate, glycolate and oxalate) (Fytianos et al., 2016). Two main degradation mechanisms are thermal degradation in presence of CO<sub>2</sub> and oxidative degradation. In this project, DORA, a technology for controlling oxidative degradation is studied.

Several studies from pilot plant operation using monoethanolamine (MEA) show that out-of-control solvent loss due to degradation makes further operation impossible after a period of operation. The main factors controlling the rate of oxidative degradation are the dissolved oxygen content, temperature and solvent residence time in specific parts of the plant (Dhingra et al., 2017). Therefore, solutions aiming to reduce the dissolved oxygen content would decrease oxidative degradation and reduce the cost of CO<sub>2</sub> capture.

The solvent is exposed to oxygen in the absorber packing and the oxygen-rich solvent is collected in the absorber sump at temperatures of ca. 50–60 °C. Already at these conditions, the dissolved oxygen will start to cause oxidative degradation. In the cross heat-exchanger, downstream of the sump, the solvent is exposed to high temperatures (typically around 100 °C), accelerating the degradation reactions between dissolved oxygen and solvent molecules.

DORA (Dissolved Oxygen Removal Apparatus) is a membrane system used to remove dissolved oxygen from CO<sub>2</sub> capture solvents. TNO

proposed the technology within the ALIGN–CCUS project (patent filed), where it was brought to TRL5 (Monteiro et al., 2018). To date, a commercially available porous membrane contactor and a lab-size membrane with a thin dense coating are tested. The porous membrane contactor was a Liqui-Cel® module packed with polypropylene hollow fibres with 25% porosity, effective pore size of 0.04 µm and corresponding inner and outer diameter of 200 and 300 µm, respectively. The lab-size dense membrane of permeating area of 8.1 cm<sup>2</sup> was developed by NTNU in the Norwegian research project 3GMC and transferred to TNO for DORA testing under the NCCS project.

DORA can be operated in liquid-liquid (L-L) or in liquid-gas (L-G) mode. The CO<sub>2</sub> capture solvent, containing dissolved oxygen, flows through the retentate (tube) side of the membrane. On the permeate (shell) side, either a liquid or a gas is used. In the L-L mode, the solvent is contacted through the membrane interface with a solution containing an oxygen scavenger, whereas in the L-G mode, a sweeping gas is used. The oxygen in the solvent is de-solubilized, and transported to the membrane's permeate side, where it is absorbed in the liquid and reacted with the scavenger (L-L) or swept by an oxygen-free gas (L-G), which can be nitrogen or even (captured) CO<sub>2</sub>.

Within ALIGN–CCUS and NCCS projects, the membrane was operated in both L-L and L-G modes at TNO facilities. More straightforward operation and more effective oxygen removal were observed in the L-G mode; therefore, this mode has been the focus of the technology development. Besides that, as part of a Dutch funded project, DORA was operated at a pilot facility in Rotterdam, PlantOne. In that project, DORA was retrofitted in the TNO mobile capture plant (Miniplant) and was used to remove oxygen continuously from the rich solvent line, while the plant captured CO<sub>2</sub> from the exhaust gas of a diesel engine. The target was to demonstrate DORA at relevant industrial environment during a long-

term campaign, to bring the technology to TRL6. Along with that, the lab experiments and pilot campaigns enabled the development of a model to predict mass transfer resistances and determine the area required for the removal of various percentages of dissolved oxygen.

## 2. Methodology

### 2.1. DORA tests at lab environment using a porous membrane

DORA was retrofitted at TNO's Miniplant (mobile CO<sub>2</sub> capture plant with capacity of ca. 1 kg CO<sub>2</sub>/h at continuous operation). The Miniplant enables tests of different solvents, multiple technologies for solvent management (oxygen removal, iron removal) and process quality control under realistic conditions at TRL5. The rig can be operated with artificial or real flue gas. . During the lab tests, artificial flue gas was used, consisting of a mixture of air and CO<sub>2</sub> (11%). An evaporator was used to saturate the gas at 40 °C before entering the absorber. The gas outlet of the absorber column is connected to a flow metre and an FTIR to allow for quantification of emissions and also enable the calculation of capture rate. On the stripper side, an electrical heater is used in the reboiler and the gas outlet is monitored with the use of a mass flow metre and a CO<sub>2</sub> analyser. The absorber is a packed bed column with an internal diameter of 0.045 m and 5 packed sections with height of 0.86 m per section, using Sulzer BX packing. During the operation the total gas flow was around 2 Nm<sup>3</sup>/h, whereas the solvent (aqueous solution of 30wt% monoethanolamine) circulation rate was set at 15 kg/h. The average rich loading obtained was 0.28 molCO<sub>2</sub>/mol MEA (standard deviation: 0.09). It was decided to use a lower rich loading to enable a higher concentration of dissolved oxygen. The pressure was regulated at 1.9 bar at the top of the stripper, and the reboiler was operated at 120 °C, which resulted in a lean loading of 0.13 molCO<sub>2</sub>/mol MEA (standard deviation: 0.044). The absorber was not equipped with a water wash section. Instead, a packed section of 0.86 m at the top of the absorber, with active cooling on the walls, controlled the gas outlet temperature to ca. 35 °C, thus reducing volatile solvent and water losses during the campaign.

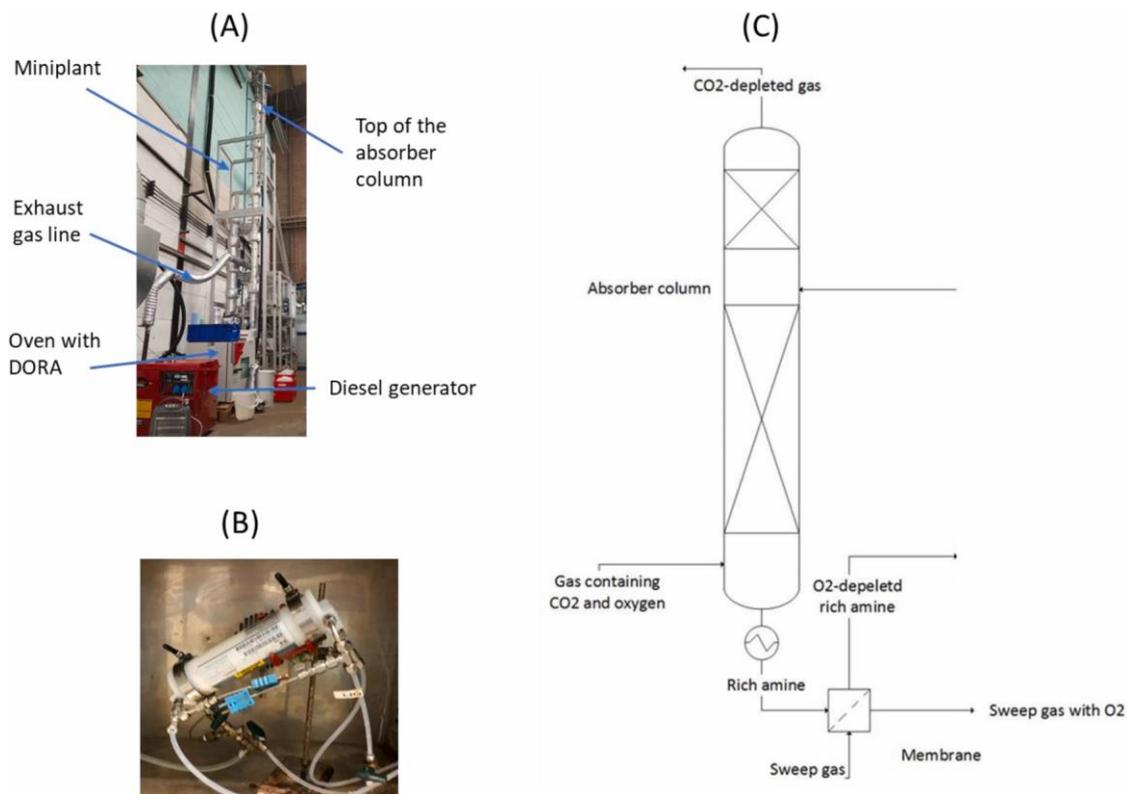
The DORA was placed after the absorber sump in the rich line in a bypass loop to enable operation with and without the membrane. This bypass loop was inside an oven, with controlled temperature at 40 °C (see Fig. 1B, C).

The membrane used in these tests was a membrane contactor module from Liqui-Cel®, from Liqui-Cel™ SP Series (2.5 × 8 extra-flow model), which consists of polypropylene hollow fibers with 25% porosity. An oxygen sensor was placed after the DORA. A commissioning campaign with artificial flue gas was performed at TNO's lab. This campaign was part of ALIGN-CCUS project and received degraded MEA solvent produced at the RWE pilot plant, connected to the Niederaussem coal-fired power plant (Moser et al., 2020). The solvent used in the Miniplant was a combination of 67% fresh solvent (MEA 30% wt) and 33% degraded solvent collected at RWE to help accelerate the degradation. Although the campaign was performed with artificial flue gas, the solvent and membrane were still exposed to impurities typical of industrial operations due to the use of degraded solvent from RWE. Online monitoring of the absorber outlet gas composition (FTIR) was done to follow the increase of ammonia emissions. Daily liquid samples were taken to control the CO<sub>2</sub> loading and the amine concentration in the solvent. The operation of DORA at TNO brought the technology to TRL5 and served as preparation for testing in industrial environments.

## 2.2. DORA operation at industrial environment using a porous membrane

For the operation at an industrial environment, the Miniplant equipped with the DORA system was transported to the PlantOne facility (Rotterdam). There, a diesel generator was used as source of flue gas (Fig. 1A) and a quench and a gas filter were installed in between the generator and the Miniplant to capture soot from the gas before entering the plant at 40 °C. This measure helps preventing emissions of MEA, which increase significantly in the presence of aerosols in the gas. The amount of CO<sub>2</sub> present in the gas coming out of the generator was around 4% which is representative of natural-gas fired boilers and furnaces. In the current project, we targeted a higher CO<sub>2</sub> content, to facilitate reaching a rich loadings of 0.5 mol/mol (which is representative of industrial cases with full height columns). Therefore, CO<sub>2</sub> cylinders were placed in the line to be able to increase the concentration to 12% and run the plant at a preferred condition. The flowrate of the flue gas inlet to the Miniplant was about 1.5 Nm<sup>3</sup>/h, whereas the solvent (again aqueous solution of 30wt% monoethanolamine) circulation rate was set at 15 kg/h. During the operation, the average obtained rich loading was 0.50 mol CO<sub>2</sub>/mol MEA (standard deviation: 0.013). The pressure was regulated at 1.9 bar at the top of the stripper, and the reboiler was operated at 120 °C, which resulted in an obtained lean loading of 0.36 mol CO<sub>2</sub>/mol MEA (standard deviation: 0.033).

The operation was divided in different campaigns that included the operation of the Miniplant with the DORA and without the DORA to compare the efficiency of the technology. The DORA system was placed in a line that could be bypassed so that by switching valves, DORA could be easily “turned on and off”. For those tests, the membrane contactor from Liqui-Cel® described in Section 2.1 was used. A gas analyser (FTIR) was connected to the absorber outlet measuring the levels of ammonia, MEA and CO<sub>2</sub> emissions. Liquid samples were taken to control the



**Fig. 1.** (A) overview of the Miniplant installation on site; (B) the DORA membrane inside the oven; (C) schematic representation of the DORA placement in the rich amine line (the heat exchanger represents the oven). loading and solvent concentration and to monitor the accumulation of acids and iron in the solution. Ammonia emissions, accumulation of acids and iron in the capture solution are all indications of solvent degradation.

### 2.3. DORA tests at lab environment using a dense layer membrane

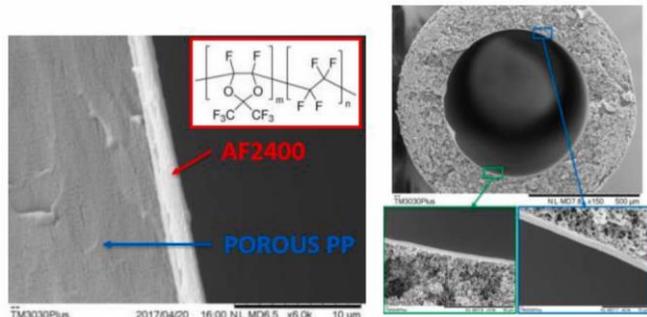
Using a dense membrane could be a better option for the DORA technology, as this could help avoid losing the solvent through the membrane. Therefore, other membrane materials are considered.

A composite membrane was developed at the Norwegian University of Science and Technology (NTNU) in Trondheim, Norway. This composite membrane (hereby referred to as the “NTNU membrane”) was fabricated by coating a perfluoropolymer (Teflon® AF2400) on top of a commercial porous polypropylene support layer (Celgard®2400). Subsequently, the same concept was transferred to PP-based hollow fibre (HF) membranes (Accurel PP Q3/1) (Andreassen, 2018). The membrane was initially designed for absorbing CO<sub>2</sub> from a gas into a liquid phase comprised of aqueous amines (Andreassen, 2018). The dense perfluoropolymer layer has a larger CO<sub>2</sub> selectivity as compared to amines thereby preventing leakages and amine emissions observed with porous membranes, Fig. 2.

As shown in Fig. 2, the HF membranes had an outer diameter of 1 mm and an inner diameter of 600 μm (porosity approximately 70%). The coating was applied in the inner wall of the HF and the dense coating thickness was approximately 1 μm (Ansaloni et al., 2019).

It was determined that NTNU’s composite membrane would be a good material candidate for DORA. A module of this membrane was obtained from NTNU and tested at TNO (as part of the NCCS project). These tests are described next.

This composite membrane was used as the membrane contactor as part of the DORA concept. In this adaptation, the membrane is expected to selectively remove oxygen from the amine, thereby controlling oxidative degradation of the solvent, while avoiding amine losses



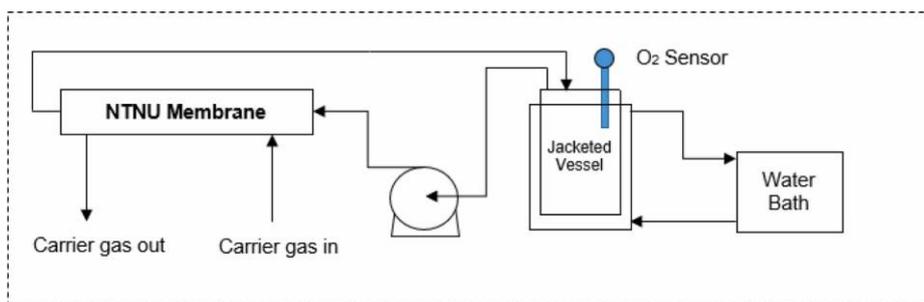
**Fig. 2.** Cross sectional image of the hollow fibre membrane with AF2400 coating (Ansaloni et al., 2019).

through the membrane. Experiments were performed at the laboratory scale to characterise the membrane for modelling purposes. The setup consisted of a jacketed vessel with an inner volume of 1.3 L with a dissolved oxygen (DO) sensor, and an inlet and outlet line to the membrane, Fig. 3. The jacket was connected to a water bath allowing for temperature control of the solvent in the vessel. Solvent was pumped through the membrane and returned to the vessel, stirred with a magnetic stirrer to ensure the liquid's uniformity.

### 3. Results and discussions of experimental work

#### 3.1. Validation of Dora with TNO's Miniplant using a porous membrane

The first campaign realized with the DORA coupled with TNO's Miniplant was done at TNO facilities using a mixture of 10% degraded solvent from RWE and 90% fresh MEA solution as a solvent to



**Fig. 3.** Schematic of laboratorial setup for dense membrane tests.

accelerate the degradation. Daily liquid samples were taken for analysis of CO<sub>2</sub> loading, MEA and water concentration. Ammonia levels measured, by the FTIR, at the gas outlet of the absorber were used as a degradation indicator. The ammonia emissions during this 2-month campaign are shown in Fig. 4. DORA operation was started when the solvent was already degraded and resulting in ammonia emissions of approximately 30 mg/m<sup>3</sup>.

During the first month of DORA operation, the ammonia levels stabilized and were below 100 mg/m<sup>3</sup>. After this period DORA was by-passed which had an immediate impact on the ammonia profile and the emissions increased to values around 100–150 mg/m<sup>3</sup>. A second campaign was done using the DORA with partial replacement of the used solvent with fresh solvent to maintain capture rate and

solvent quality. The ammonia levels dropped to around 50 mg/m<sup>3</sup> and were stable during the entire operation.

### 3.2. DORA campaign at industrial environment using a porous membrane

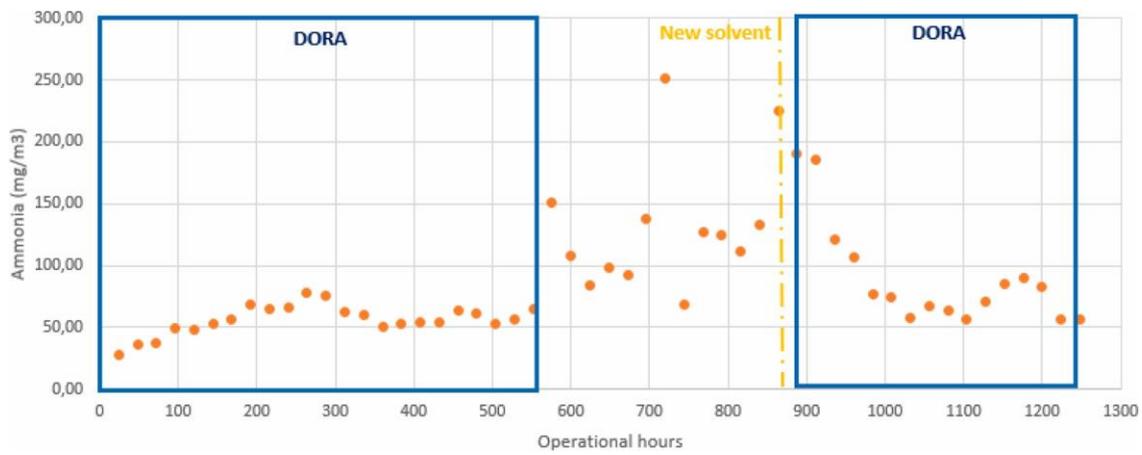
The DORA was connected to the rich line after the absorber with a bypass connection. The operation planned to occur in L-G mode using nitrogen as sweeping gas and the DORA was in total operated for around 500 h (not consecutively) to see if any influence was observed in the ammonia emissions. No transfer of nitrogen to the amine solvents was observed during this campaign.

#### 3.2.1. Operation with the Dora

Fig. 5 shows the results of this operation and represents ammonia emissions, in mg/h, from the absorber outlet and the gas outlet of the DORA. It is vital to measure the DORA outlet to show that any eventual decrease in ammonia levels is due to control in the degradation and not stripping of ammonia from the DORA itself. This picture shows that the amount of ammonia that slips through the DORA membrane is negligible (a maximum of 1,5 mg/h was registered). The results are given in mg/h in order to allow the direct comparison between the measurements in the outlet of the absorber and of the DORA (as the gas flowrates are different, reporting in mg/Nm<sup>3</sup> would not allow for that).

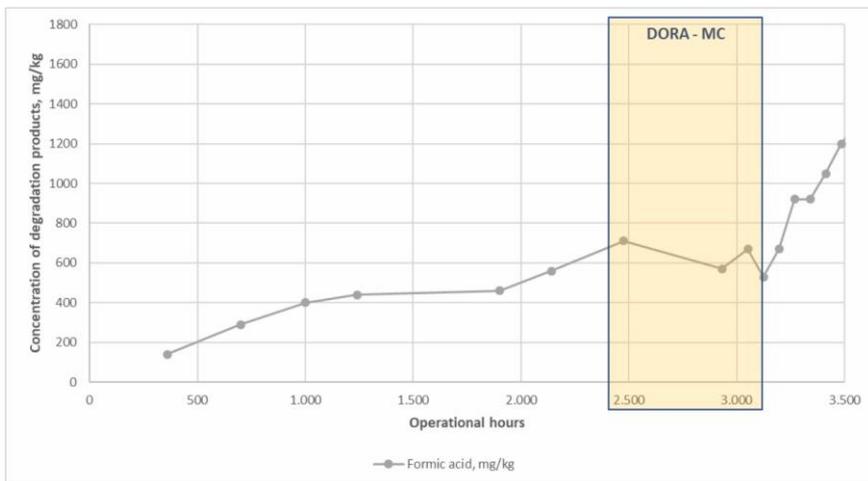
In the first cycle in which DORA is turned on, there is an apparent decrease of ammonia emissions. Considering the average of both periods, this decrease was only 10%. There was a two week stop in operation. During this time some fresh solvent was added to increase the solvent concentration, maintain capture rate and provide the necessary inventory to operate the plant. When the plant was restarted the ammonia emission level went up. The ammonia levels were higher even when the DORA was on (after 2000 h of operation). Based on the ammonia results, it is challenging to estimate how well DORA was functioning. This can be attributed to variation in operating conditions and quality of flue gas which lead to high variations in ammonia levels. To better understand the performance of the membrane solvent samples were analysed to track the formation of degradation products. Additionally, the membrane was also evaluated after the campaign to further assess its performance. This evaluation is presented in section 3.3.

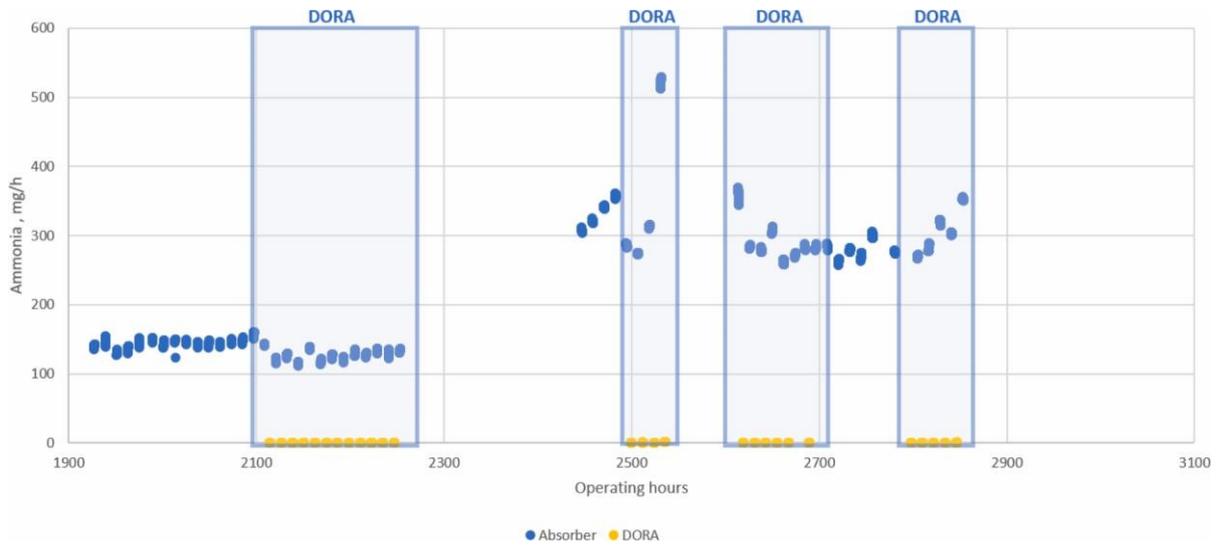
Figs. 6 and 7 show the content of three degradation products, formate, acetate (expresses as their acids) and oxalate, as determined from liquid solvent samples sent to an external lab for analysis. These are oxidative degradation products formed from MEA (which then further degrade to ammonia). These figures are plotted against the operational hours of the Miniplant. The yellow rectangles indicate the period in which DORA was operational. It should be emphasized that, as shown above (in Fig. 4), the DORA operation wasn't continuous – in fact, in the period indicated, the DORA availability was ca. 37%. Nevertheless, the graphs show that the operation of DORA has a clear impact on the degradation of MEA, controlling the composition of the key oxidative degradation products. From the start of the campaign until almost 2500 h, a steady increase in the concentrations of formate, acetate and oxalate is observed. Then, for about 700 h, the concentrations remain constant. And after DORA is by-passed, the concentrations start to increase rapidly. The increased rate of formation of the degradation products is in



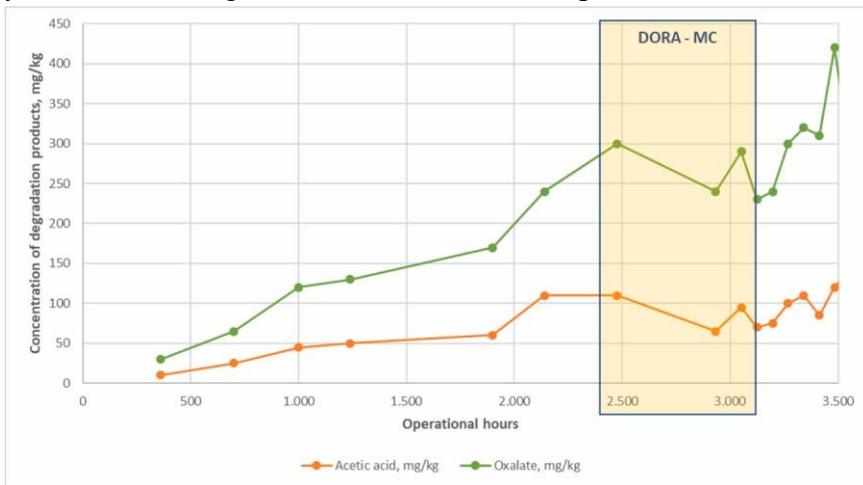
**Fig. 4.** Operation in the CO<sub>2</sub> capture Miniplant with and without the DORA.

**Fig. 5.** DORA operation integrated in the Miniplant, ammonia emissions in mg/h.





**Fig. 6.** DORA operation integrated in the Miniplant, formate content (expressed as formic acid). The yellow rectangle indicates the period in which DORA was operational.



**Fig. 7.** DORA operation integrated in the Miniplant, acetate (expressed as acetic acid) and oxalate contents.

line with exponential increase reported by long term campaigns with 30wt% MEA at post combustion pilot facilities at Niederaussem in Germany and at the Technology Centre Mongstad in Norway (Ansaloni et al., 2019)[7].

These results brought DORA to TRL6. The technology was demonstrated at relevant environment. The flue gas impurities and the oxygen content, and the operational conditions achieved at the Miniplant are representative of full scale industrial CO<sub>2</sub> capture facilities. DORA was shown to control the formation of degradation products.

Estimating the impact of DORA on solvent losses based on the solvent mass balance during the campaign at industrial environment was not possible. Due to the high content of aerosol particles, high aerosol-based solvent losses were experienced, and extensive solvent make-up was needed during the campaign

### 3.3. Testing of different membranes with degraded solvent at lab scale

After the operation of the Liqui-Cel® membrane contactor with the Miniplant at the industrial facility, the membrane appeared to be damaged, due to significant reduction in removal efficiency. In order to verify this hypothesis, the membrane was tested in the setup described in Fig. 3. These tests were done with the degraded solvent from the Miniplant (previously filtered). The NTNU membrane was also tested with the same solvent to determine whether this membrane also would work on an already degraded sample in presence of metallic impurities.

The results of the tests clearly indicate the difference between the NTNU membrane and the used (damaged) Liqui-Cel® membrane. The oxygen removal rate from the damaged Liqui-Cel® membrane was practically identical to the rate with no membrane. This indicates that even when the damaged Liqui-Cel® membrane is employed the rate of oxygen decay corresponds only to the rate at which it is consumed by the solvent, in other words, no actual separation is achieved. An explanation for this could be that the Liqui-Cel® had been damaged to the point of losing its mass transfer capabilities (e.g., due to pore clogging) during operation at the industrial environment.

Conversely, the test performed with the NTNU membrane showed promising results removing oxygen from the amine solution at an increased rate compared to the two other tests and lowering the oxygen content from 20 mg/L to below 1 mg/L three times faster than with the Liqui-Cel® or with no membrane. Comparison is shown in Fig. 8. The NTNU membrane has since been tested for over a year by TNO in the laboratory and no physical damage to the membrane or coating has been observed.

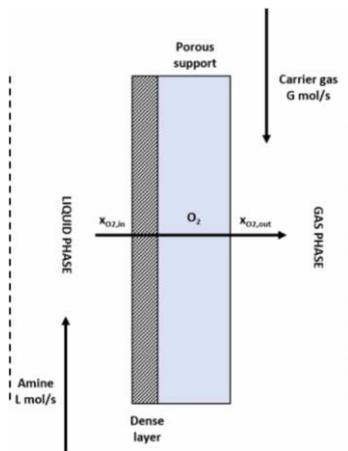
## 4. DORA modelling

Laboratory tests were carried out with the dense layer membrane, developed by NTNU, and a model was developed to describe the mass transfer of dissolved oxygen from the solvent to the carrier gas. This model was also used to size the membrane for different oxygen removal rates using this membrane. Fig. 9 shows a schematic of the membrane operation in the L-G mode.

The oxygen-containing aqueous amine solvent flows along the dense layer of the membrane at a flow rate of  $L \text{ mol.s}^{-1}$ . On the porous side a carrier gas (nitrogen or carbon dioxide) removes the oxygen continuously at a flow rate of  $G \text{ mol.s}^{-1}$ . The flux of oxygen removed from the membrane can be expressed as:

$$\left( \right) \\ x_{O_2,in} - x_{O_2,out} L N_{O_2} = \text{_____} A$$

Where  $N_{O_2}$  is the oxygen flux per unit area measured in  $\text{mol.m}^{-2}.\text{s}^{-1}$ ,  $x_{O_2,in}$  and  $x_{O_2,out}$  are the mole fractions of oxygen in the inlet and outlet of the membrane contactor, and  $A$  is the permeating area in  $\text{m}^2$ .



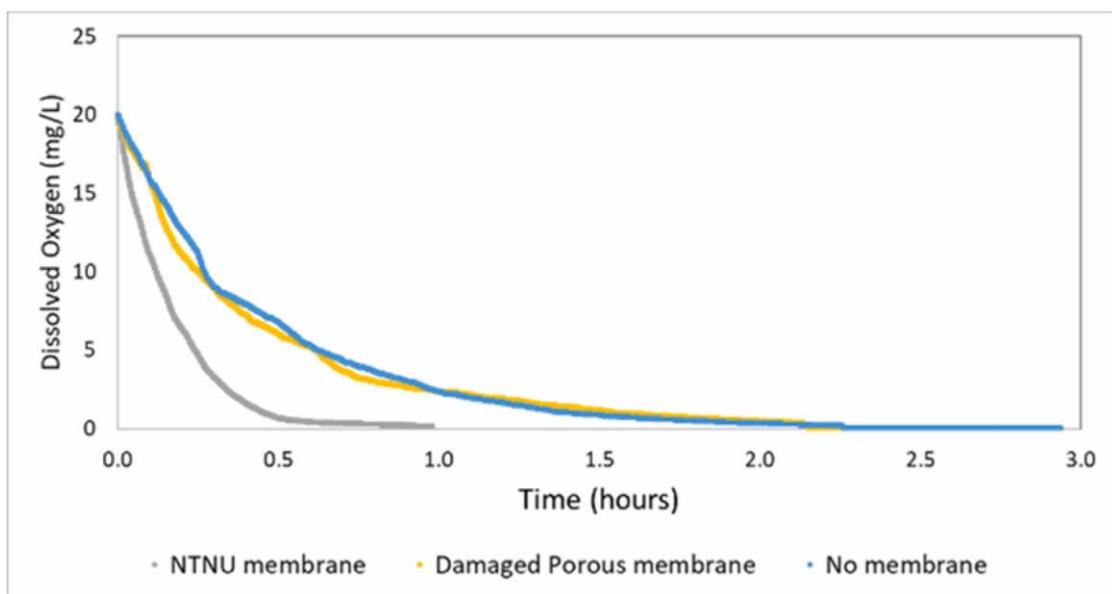
**Fig. 9.** Dense layer membrane for dissolved oxygen removal.

The mass transfer of oxygen from the liquid phase through the membrane contactor and to the gas phase can be described using the resistance in series model. The overall mass transfer resistance has a contribution from the liquid phase, membrane (dense layer and porous support) and the gas phase. The overall mass transfer resistance can be expressed as follows.

$$\frac{1}{K_{ov}} = \frac{1}{K_l} + \frac{1}{K_m} + \frac{1}{K_g}$$

Where  $K_{ov}$  is the overall mass transfer coefficient and  $K_l$ ,  $K_m$  and  $K_g$  are the mass transfer coefficients for the liquid phase, membrane and the gas phase. The overall mass transfer coefficient can also be expressed as:

$$K_{ov} = \frac{x_{O2,in} - x_{O2,out}}{\Delta CO_{2,LM}} = \frac{1}{\frac{1}{K_l} + \frac{1}{K_m} + \frac{1}{K_g}}$$



**Fig. 8.** Oxygen removal/degradation rates of Liqui-Cel®, the NTNU membrane and the set-up with no membrane.

Where  $\Delta_{CO_2,LM}$  is the log mean concentration difference and is calculated using the concentration difference at the inlet ( $\Delta_{CO_2,in}$ ) and outlet ( $\Delta_{CO_2,out}$ ). It is assumed the carrier gas removes oxygen in the gas phase instantaneously thereby maximizing driving force. Thus, the gas side mass transfer resistance can be ignored. This can always be achieved in the operations, by assuring that the gas flowrate is sufficiently large.

#### 4.1. Membrane mass transfer

The mass transfer resistance offered by the membrane has two components: resistance offered by the porous support and that offered by the dense layer. The mass transfer coefficient through the porous membrane ( $k_{ps}$ ) is a function of the diffusivity through the membrane pores ( $D_{O_2,p}$ ), porosity ( $\epsilon$ ) and tortuosity ( $\tau$ ) of the membrane, and the membrane thickness ( $\delta_{ps}$ ) (Su, 2018).

In a porous membrane, the diffusion of oxygen is governed by Knudsen diffusion and the diffusivity through the pores can be calculated using the following equation (Ismail et al., 2015):

$$D_{O_2,p} = \frac{1}{3} \frac{d_p}{\tau} \sqrt{\frac{8RT}{\pi M_w}}$$

Where  $d_p$  is the mean pore diameter of the porous support,  $R$  is the universal gas constant,  $T$  is the temperature in K and  $M_w$  is the molecular weight of oxygen. At 40 °C, the diffusivity of oxygen through the HF porous support was calculated using the equation above as  $6.53 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ . Using this diffusivity of oxygen through the porous membrane, the mass transfer coefficient through the porous layer ( $k_{ps}$ ) is calculated as  $7.4 \times 10^{-2} \text{ m} \cdot \text{s}^{-1}$ .

Mass transfer through the dense layer of the perfluoropolymer is dependant on the thickness of the layer ( $\delta_{dl}$ ) and the permeability of oxygen through this layer ( $P_{O_2}$ ). The mass transfer coefficient ( $k_{dl}$ ) through the dense layer is estimated using the following equation:

$$k_{dl} = \frac{P_{O_2}}{\delta_{dl} v_m}$$

Here  $v_m$  is the molar volume of oxygen. At 40 °C, the molar volume of oxygen was calculated as  $2.6 \times 10^{-2} \text{ m}^3 \cdot \text{mol}^{-1}$ . The permeability of oxygen through the dense layer is determined as follows (Nagy, 2019), (Ansaloni et al., 2017):

$$J_{O_2} = k_{dl} (p_{O_2,l} - p_{O_2,g})$$

$$k_{dl} = \frac{J_{O_2}}{p_{O_2,l} - p_{O_2,g}}$$

Where  $J_{O_2}$  is the flux of oxygen through the membrane, and  $p_{O_2,l}$  and  $p_{O_2,g}$  are the partial pressures of oxygen on the liquid and gas side, respectively.

Henry's constant for oxygen in the amine was experimentally determined to be  $6.82 \text{ mg} \cdot \text{l}^{-1}$  when 30 wt% MEA was loaded with air at 40 °C.  $p_{O_2}^*$  is the saturation pressure of oxygen and  $x_{O_2}$  is the saturation concentration of oxygen in the liquid. Based on this information, the permeability of oxygen was estimated to be 418.7 Barrer (where  $1 \text{ Barrer} = 3.35 \times 10^{-16} \text{ mol} \cdot \text{m}^{-1} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ ). Based on the permeability of oxygen through the dense layer, the mass transfer coefficient through the dense layer ( $k_{dl}$ ) is calculated as  $40.47 \text{ m} \cdot \text{s}^{-1}$ , which makes the mass transfer resistance through the dense layer negligible as compared to that of the porous support.

The total mass transfer coefficient through the membrane ( $K_m$ ) is calculated as follows:

$$\frac{1}{K_m} = \frac{1}{k_p} + \frac{1}{k_d}$$

The mass transfer coefficient through the membrane is  $1.74 \times 10^{-2} \text{ m.s}^{-1}$ .

#### 4.2. Liquid film mass transfer

The mass transfer coefficient through liquid film ( $K_l$ ) can be expressed as:

$$\frac{1}{K_l} = \frac{1}{m E k_l}$$

Where  $m$  is the partition coefficient,  $E$  is the Hatta number that quantifies the effect of chemical reaction and  $k_l$  is the liquid physical mass transfer coefficient (Celgard LLC 2009). The Hatta number for a reaction of order  $m$  is estimated using the following equation.

$$E = \frac{k_m C_{O_2} - 1}{D_{O_2, l} m + 1}$$

Degradation experiments were conducted at TNO to determine the rate ( $k_m$ ) and order ( $m$ ) of reaction for oxygen consumption in 30 wt% MEA. It was determined that the consumption of oxygen is a half order reaction ( $m = 0.5$ ) with rate constant  $0.0011 \text{ mol}^{0.5} \text{ l}^{0.5} \text{ s}^{-1}$ . The diffusivity of oxygen in the liquid can be calculated from diffusivity of water ( $D_{O_2, w}$ ) and the viscosities of the liquid ( $\mu_l$ ) and water ( $\mu_w$ ).

$$\left( \frac{\mu_w}{\mu_l} \right)^{0.6} D_{O_2, l} = D_{O_2, w}$$

On the basis of these equations the mass transfer coefficient ( $K_l$ ) was calculated to be  $6.16 \times 10^{-4} \text{ m.s}^{-1}$ .

#### 4.3. Overall mass transfer

The overall mass transfer coefficient was calculated as:

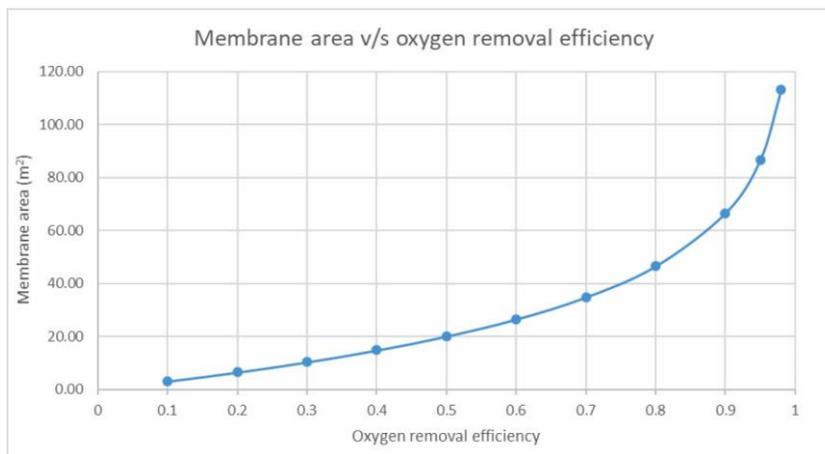
$$\frac{1}{K_o} = \frac{1}{K_l} + \frac{1}{K_m}$$

From the mass transfer coefficients for the membrane and liquid, the overall mass transfer coefficient was calculated as  $5.95 \times 10^{-4} \text{ m.s}^{-1}$ . The main resistance to mass transfer is on the liquid film. This mass transfer resistance can be used to scale up and size the membrane for higher flow rates.

#### 4.4. Membrane scale up

The model above was used to size the dense layer membrane for a hypothetical  $\text{CO}_2$  capture pilot plant with a solvent flow rate of  $15 \text{ m}^3/\text{h}$ . The membrane area ( $A_m$ ) required for oxygen removal efficiency of  $\eta$  can be calculated as:

$$A_m = \frac{\eta \times O_{2, inL}}{K_o \Delta \text{CO}_{2, LM}}$$



**Fig. 10.** Membrane area needed for different oxygen removal efficiencies.

Assuming operation at 40 °C and oxygen solubility of 6.31 mg.l<sup>-1</sup>, a membrane of size 67m<sup>2</sup> will lead to 90% oxygen removal. Fig. 10 shows the different membrane sizes needed for different oxygen removal efficiencies. Membranes of the calculated scale are readily available commercially and can be easily retrofitted to existing installations.

## 5. Conclusions

This work describes the operation of TNO’s mobile CO<sub>2</sub> capture plant at lab and industrial environments for the demonstration of a degradation mitigation technology – DORA. This technology was proposed by TNO within the ALIGN–CCUS project (from TRL0 to TRL5), and demonstrated at TRL6 at an industrial site (PlantOne). The PlantOne campaign lasted around 3600 h, using 30wt% MEA as solvent. The concentration of degradation products (formate, acetate, oxalate) in the solvent increased from the start of the operation. When the formate content reached around 700 mg/kg of solvent (ca. 2400 operational hours), the DORA system was put online. It was operated intermittently for about 700 h (availability of 37%), and during this time the concentration of degradation products remained constant. When DORA was bypassed, the increase in the concentration of the degradation products resumed. This indicates that technology works as intended – by removing dissolved oxygen from the solvent, the degradation process is greatly decelerated, and the composition of the solvent can be kept stable.

For the tests at PlantOne, a porous membrane contactor (LiquiCel®) was used. After the DORA campaign, the membrane was disconnected from the rich solvent line, but remained filled with stagnant solvent. This damaged the membrane, as demonstrated in lab tests performed afterwards, showing that no capacity for oxygen mass transfer capacity was left, likely due to clogging of the pores. While the membrane operated well for ca. 700 h, we can conclude that porous membrane contactors are not the preferred solution for the DORA technology, due to the risk of operational issues such as clogging and wetting of the pores. Particularly with degraded solvent, when the surface tension drops, solvent may leak through the membrane. Besides that, porous membrane contactors offer little resistance to the mass transfer of volatile solvents (such as MEA), and can lead to solvent losses.

To mitigate this and search for a viable solution for the DORA technology, TNO has performed lab tests (TRL4) with a membrane developed by NTNU. This membrane has a dense layer coating, which avoids leakages and improves the oxygen selectivity over solvent.

A model was developed for the NTNU membrane using a resistance in series model. Based on this model, it is evident that the liquid phase resistance is the dominant factor limiting oxygen transfer. This indicates that the membrane characteristics are already satisfactory, and that a scaled-up solution based on the current technology can be investigated.

The required permeating area is a function of the oxygen removal efficiency and increases with the amount of oxygen removed.

Currently, thermal reclaiming is the benchmark solvent management technique to control the level of heat stable salts in the solvent. However, reclaiming large volumes of degraded solvent leads to increased costs associated with operation and waste handling. DORA reduces the extent of oxidative degradation, thereby, decreasing the volume of solvent that needs to be reclaimed. This, in turn reduces the operational costs and the environmental impacts of CO<sub>2</sub> capture processes.

In conclusion, DORA is potentially a technically and economically viable solution for controlling the degradation of CO<sub>2</sub> capture solvents and can be applied independently or in combination with other solvent management strategies such as reclaiming.

### **CRedit authorship contribution statement**

**Roberta V. Figueiredo:** Conceptualization, Validation, Investigation, Writing – original draft, Visualization. **Tanya Srivastava:** Conceptualization, Validation, Formal analysis, Data curation, Writing – original draft. **Tarjei Skaar:** Investigation. **Niels Warning:** Investigation. **Paul Gravesteijn:** Investigation. **Peter van Os:** Writing – review & editing, Supervision, Project administration. **Luca Ansaloni:** Resources, Writing – review & editing. **Liyuan Deng:** Resources, Writing – review & editing. **Hanna Knuutila:** Resources, Writing – review & editing. **Juliana Monteiro:** Conceptualization, Methodology, Validation, Data curation, Writing – review & editing, Supervision. **Earl Goetheer:** Conceptualization, Supervision.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### **References**

- Fytianos, G., Vevelstad, S.J., Knuutila, H.K., 2016. Degradation and corrosion inhibitors for MEA-based CO<sub>2</sub> capture plants. *Int. J. Greenh. Gas Control* 50, 240–247. <https://doi.org/10.1016/j.ijggc.2016.05.003>. Supplement C.
- Dhingra, S., et al., 2017. Understanding and modelling the effect of dissolved metals on solvent degradation in post combustion CO<sub>2</sub> capture based on pilot plant experience. *Energies* 10 (5), 629. <https://doi.org/10.3390/en10050629>. May.
- J.G.M.-S. Monteiro et al., “De-oxygenation as countermeasure for the reduction of oxidative degradation of CO<sub>2</sub> capture solvents,” 2018.
- Moser, P., et al., 2020. 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* 95, 102945. <https://doi.org/10.1016/j.ijggc.2019.102945>.
- Andreassen, V.E., 2018. Carbon Dioxide Absorption With Non-Porous Hollow Fiber Membrane Contactors – Module fabrication and Characterization. NTNU retrieved from. <https://ntnuopen.ntnu.no/ntnu-xmlui/handle/11250/2615720>.
- Ansaloni, L., Hartono, A., Awais, M., Knuutila, H.K., Deng, L., 2019. CO<sub>2</sub> capture using highly viscous amine blends in non-porous membrane contactors. *Chem. Eng. J.* 359 (2019), 1581–1591. <https://doi.org/10.1016/j.cej.2018.11.014>.
- Celgard LLC, 2009. Product Specifications: Commercial Monolayer & Specialty Products. Celgard LLC.
- Su, J., 2018. Effects of vacuum and flow rate on water deoxygenation through Tri-Bore PVDF hollow fiber membranes. *SF J Mater. Chem Eng.* 1 (2), 2018, 1.
- Nagy, E., 2019. Chapter 11 - Membrane Contactors. *Basic Equations of Mass Transport Through a Membrane Layer*, 2nd ed. Elsevier, pp. 337–345. E. B. T.-B. E. of M. T. T. a M. L. (Second E. Nagy, Ed.
- Ansaloni, L., Rennemo, R., Knuutila, H.K., Deng, L., 2017. Development of membrane contactors using volatile amine-based absorbents for CO<sub>2</sub> capture: amine permeation through the membrane. *J. Memb. Sci.* 537, 272–282. <https://doi.org/10.1016/j.memsci.2017.05.016>.
- A.F. Ismail, K.C. Khulbe, and T. Matsuura, “Fundamentals of gas permeation through Membranes BT - Gas separation membranes: polymeric and inorganic,” A.F. Ismail, K. Chandra Khulbe, and T. Matsuura, Eds. Cham: Springer International Publishing, 2015, pp. 11–35.