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Demonstrating a Refinery-adapted cluster-integrated strategy
to enable full-chain CCUS implementation - REALISE

D1.2 Solvent Management Strategy

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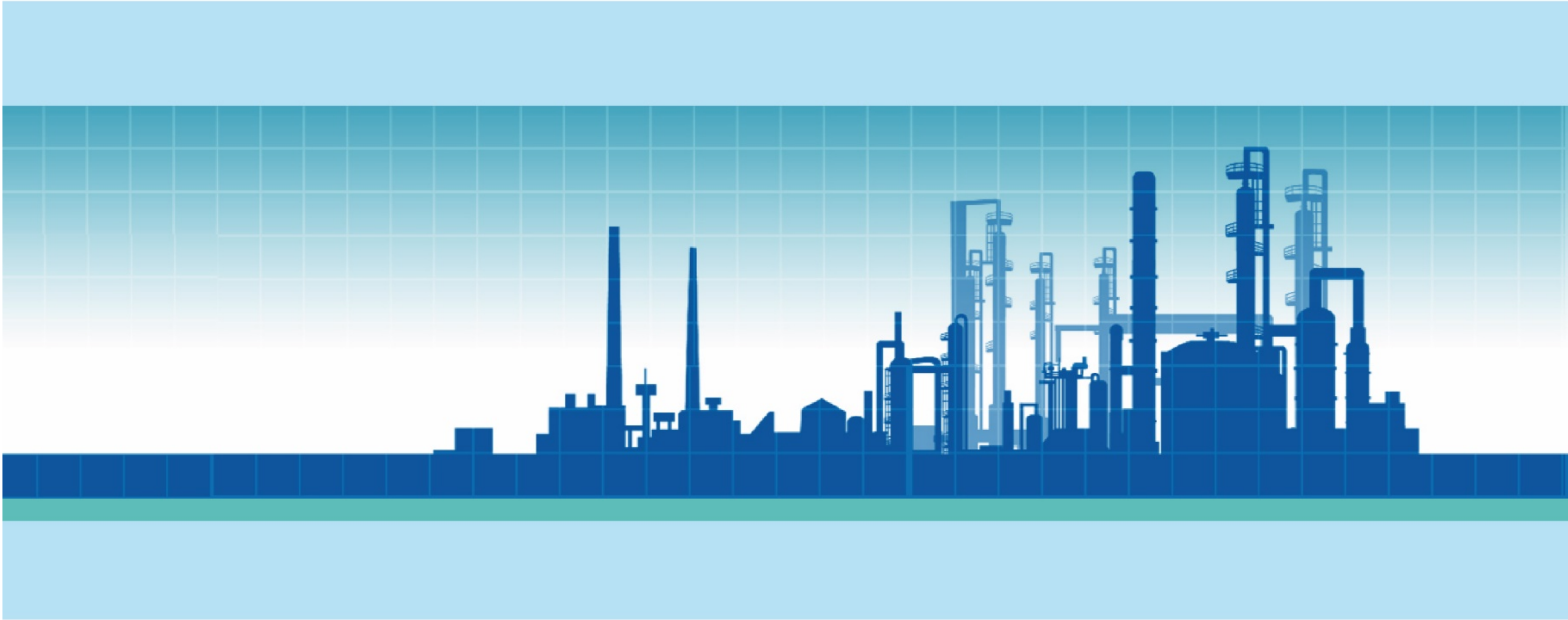

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Executive summary

Amine based CO_2 capture is a key technology for achieving climate goals. However, its wide scale implementation is hampered by degradation of amines which leads to adverse impacts on process economics and, to the extent of its environmental impact. Amine degradation leads to the formation of a wide variety of undesirable products (including for example, volatile components, such as ammonia, and heat stable salts) that accumulate in the solvent over time. The accumulation of these products changes solvent properties, leads to increased operational difficulties and impacts the overall process efficiency and costs. To maintain solvent performance and achieve desired capture rates overtime, it is critical to control solvent degradation.

Several solvent management strategies have been investigated to maintain solvent quality. These strategies can be either reactive or proactive. Reactive strategies are applied after the solvent has reached a predetermined degradation threshold. Reactive strategies include solvent change over, ‘bleed and feed’, and reclaiming. Proactive strategies on the other hand are applied online preferably from the beginning of operation to limit the extent of solvent degradation. Strategies such as adsorption with activated carbon and dissolved oxygen removal are proactive.

Within Task 1.2, TNO has selected three solvent management strategies for investigation to be tested in combination with the HS-3 solvent demonstration campaign within WP2 at Irving Refinery in Ireland. These are adsorption of impurities with activated carbon, dissolved oxygen removal using membranes and thermal reclaiming. The first two will be integrated in the mobile CO_2 capture plant used in the campaign, while the last one will be tested in the laboratories at TNO.

Activated carbon has been extensively used for the removal of impurities from a wide variety of industrial processes. Carbons can adsorb impurities like organics and metals from fluids. TNO has designed an activated carbon column that will use a commercial carbon for purification of the solvent. The online tests at Irving Refinery will be used to assess and quantify the impact of activated carbon on solvent degradation and to estimate the impact in process costs of using activated carbon as a solvent management strategy. In this report, the design of the column and the experimental matrix for the laboratory and field tests are presented.

Dissolved oxygen removal will also be tested by using DORA (**D**issolved **O**xygen **R**emoval **A**pparatus), an online solvent management strategy developed by TNO. DORA employs membranes for removal of dissolved oxygen from capture solvents. TNO has tested DORA using commercial porous membranes and a dense layer membrane fabricated by NTNU. Tests show that DORA is capable of removing more than 90% of the dissolved oxygen from amine solvents. The removal of oxygen leads to a reduction in oxidative degradation. This report discusses the laboratory tests that were carried out with DORA to optimize the operating conditions.

Finally, thermal reclaiming will be carried out with degraded HS-3 solvent from the campaign at Irving Refinery. Thermal reclaiming uses heat to recover amines from degraded solvents. Thermal reclaiming of single component solvents like 30wt% monoethanolamine is carried out at a single temperature. The reclaiming of a blend like HS-3 may require operation at different

temperature levels to maximize the recovery of both components while minimizing additional degradation during the reclaiming process. TNO will carry out tests at the laboratory scale with degraded HS-3 to design a method and equipment for reclaiming of amines from degraded blends. In this report, the differences between reclaiming of single component solvents and solvent blends are discussed.

Table of Contents

1 Introduction

Amine based solvents can degrade through three main mechanisms in post combustion CO_2 capture plants. These mechanism are oxidative, thermal and CO_2 induced [1] degradation. Oxidative degradation of amines occurs in the presence of oxygen and normally occurs at low temperatures (40 °C). This type of degradation results in the formation of a variety of undesirable products including ammonia, alkylamine, aldehydes and acidic compounds that can react further to form Heat Stable Salts (HSS) [2]. Presence of CO_2 influences the oxidative stability of e.g. monoethanolamine, lab-scale experiments showed large variation in chemical stability between unloaded (0 molCO_2/mol MEA) and loaded (0.4 mol CO_2/mol MEA) MEA solutions [3]. Thermal degradation on the other hand occurs at temperatures resulting in the formation of degradation products with higher molecular weights [4]. Without CO_2 presence, aqueous amine solutions have been found to be relatively stable even at 200 °C [5]. According to the third mechanism (often called carbamate polymerization reactions), primary and secondary amines react to form e.g. oxazolidones and diamines in the presence of CO_2 [1].

Solvent degradation leads to the formation and accumulation of undesirable products in the plant over time. This formation causes loss of solvent capacity which leads to the necessity for solvent replenishment to maintain desired capture rates and solvent quality [6]. The accumulation of these products also leads to changes in solvent properties like viscosity and density, and also an increase in equipment fouling and solvent corrosivity [7]. With increased corrosivity, metals (such as iron, nickel and chromium) from the materials of the construction also accumulate in the solvent. The impact of metals in solvent degradation is still a discussion point. While some plants reported a significant influence of metals on increasing solvent degradation [8], the same effect was not observed in other plants [9]. Therefore, further research is needed to get a deeper understanding of this phenomena. Fundamental research is currently being carried out in a parallel project (LAUNCH-CCUS, coordinated by TNO and with the participation of SINTEF, NTNU and Biobe). Knowledge transfer form LAUNCH helps informing the mitigation pathways taken in REALISE.

The effects of solvent degradation lead to an overall negative impact on the economics and environmental impact of amine-based post combustion CO_2 capture (PCCC). Thus, it is critical to maintain solvent quality and control the accumulation of degradation products in the plant. This can be achieved through a variety of solvent management strategies that have been discussed below.

1.1 Overview of Solvent Management

Solvent management in PCC plants can be classified into two main categories: reactive and proactive. Reactive techniques allow the solvent to degrade over time and corrective action is taken after a certain level of degradation has occurred. On the other hand, proactive techniques are applied to the plant from the beginning of operation and aim at controlling degradation.

1.1.1 Reactive Solvent Management Techniques

Several reactive solvent management techniques have been investigated for maintaining solvent quality. A brief overview of some of these strategies is provided here.

- **Change Over of Solvent Inventory:** This strategy involves the replacement of the entire solvent inventory. The decision on when to change the inventory can be based on physical characteristics like viscosity or the level of impurities in the solvent. While this method will get rid of impurities and degradation products, the disposed solvent can still contain up to 80% usable solvent. This option has a major environmental and economic impact associated with disposal of large volumes of solvent [8],[10]. Solvent removed from the plant can be reclaimed in batches later to minimize waste.
- **'Bleed and Feed':** In this strategy a small portion of the used solvent is taken out and replaced with fresh solvent to maintain the concentration of impurities below a certain level. However, this strategy like the change-over also involves disposal of useful solvent, with consequent adverse environmental and economic impacts [10].
- **Solvent Recycling and Reclaiming:** This strategy is carried out to recover amines from degraded solvents. The recovered amines are reintroduced to the capture plant. This strategy leads to reduction in waste streams, disposal costs and the associated environmental impact. Reclaiming and recycling can be carried out through different methods – ion exchange, electrodialysis, and thermal reclaiming. Solvent reclaiming can be carried out either as a reactive strategy after a certain amount of degradation products have formed or as an online proactive strategy that treats a slip stream of the solvent and prevents accumulation of degradation products and impurities, thus controlling the degradation rate. While several strategies can be easily applied to primary amines, the reclaiming of blends can be more challenging as the technique has to account for recovery of two or more components with different physical properties.

1.1.2 Proactive Solvent Management Techniques

Proactive solvent management techniques are implemented online and treat the solvent during operation. These techniques are typically used to control and reduce degradation by limiting the formation of degradation products. An overview of some proactive strategies is provided below.

- **Mechanical Filtration:** These filters are used to remove particulate impurities e.g., coming from the flue gas. However, these filters are incapable of removing heat stable salts (HSSs) and degradation products. As a result, these filters are limited in their ability to maintain solvent quality [10].
- **Activated Carbon Filtration:** Activated carbon can purify solvents by means of adsorption. The carbon is capable to removing some high molecular weight polymeric degradation products that are mainly formed as a result of carbamate polymerization reactions [10]. There is evidence of separation of metals in combination with degradation products (which act as chelating agents), which may contribute to controlling degradation. However, there are several challenges associated with these filters like under sizing, liquid distribution, replacement of carbon and difficulty in monitoring the filters' performance [11]. Additionally, the adsorption capacity of the carbon for degradation products is limited.

- **Online Neutralization:** This strategy involves the control of HSSs by means of introducing sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3) to the solvent to react with and displace the amines from the HSSs [12]. However, over time the sodium salts produced from neutralization are accumulated in the solvent and leading to an increase in viscosity and reduced solvent capacity. These issues can be overcome by combining online neutralization with reclaiming.
- **Dissolved Oxygen Removal:** Mitigation of oxidative degradation can be achieved through the removal of dissolved oxygen from the capture solvent. This removal can be achieved through the introduction of oxygen scavengers, by nitrogen sparging or using membranes [13]. These strategies are still under development and are being demonstrated at pilot scale. The other techniques mentioned above have been demonstrated at larger scales in the oil and gas industry.

1.2 Solvent Management Strategies for REALISE

Within the REALISE project, a solvent management strategy will be investigated, comprising of 3 techniques. At the miniplant, during the campaign in Ireland, activated carbon filtration and dissolved oxygen removal will be tested as proactive technologies. After the campaign, a sample of degraded solvent will be thermally reclaimed at TNO's lab (reactive technology).

With the information from the different tests, advice on an optimized solvent management strategy for HS-3 will be derived. These will inform the design of the full-scale CO_2 capture plants in WP3.

This report provides an overview of the approach for application of these technologies.

2 Activated Carbon Filtration

As mentioned in Chapter 1, degradation of amines leads to several undesirable reactions generating a wide array of compounds like organic acids, amides, amines, ring structures. The corrosivity of the solvent increases due the accumulation of these products, thereby leading to an increased metal, and in particular iron, concentration in the solvent. This increased iron level, in turn has been reported to accelerate the oxidative degradation of amines [2][14]. As a result, a ”runaway” cycle of degradation is created resulting in a snowball effect that leads to an exponential increase in degradation and adverse effects for plant operation and the environment.

It has been postulated that the removal of iron and degradation products from the capture solvent can break this cycle and slow down degradation. Activated carbon has been extensively used for iron removal in waste water systems [15]. To test if activated carbon is a viable and effective solvent management strategy, experiments will be carried out at TNO’s laboratories and online with TNO’s Miniplant operation at Irving Refinery.

2.1 Activated Carbon Column

A column was designed for the purpose of testing the effectiveness of activated carbon in controlling degradation of amines. This column was designed to handle 1% (maximum 2l/h) of the total solvent flow rate of the Miniplant which is comparable to what is usually used in operational pilots/commercial plants. Based on guidelines for designing activated carbon columns, it was decided to maintain a height to diameter ratio of 10:1 [16]. This prevents the impact of channelling and helps in maintaining a good distribution of solvent over the adsorption bed. With these parameters, a column with total height of 50 cm (activated carbon bed height of 40 cm) and diameter of 5 cm was fabricated. The column is equipped with a filter to prevent any carbon particles from entering the solvent stream. A sample point has been provided at the bottom of the column as shown below in Figure 1.

For the purpose of testing in the lab, solvent can be recirculated over the carbon bed with a pump for the desired amount of time. This column will also be connected to the Miniplant while in operation at Irving refinery. A slip stream of 10% of the rich flow will be sent to the column. The treated solvent from the bottom of the column will be pumped back to the plant. When operated online, the column will provide a residence time of between 15 and 30 minutes, depending on the solvent flow rate in the Miniplant, which is necessary for an optimal removal.

The activated carbon column will be integrated with the Miniplant after stable operation has been attained. First the Miniplant will be operated at Irving refinery without any solvent management technologies. During this time, the solvent quality and operational stability will be monitored. Once the plant operation is stable and the solvent has started to degrade, the activated carbon column will be integrated with the Miniplant.

To monitor the impact of the activated carbon column when it is operated with the Miniplant, three approaches will be taken. Offline analysis of the solvent will be used to measure the amount of impurities – in terms of degradation products and metals – in the treated solvent. These levels will be compared with those in the untreated solvent (rich solvent sample taken upstream the activated carbon column). Secondly, it is expected that the activated carbon column will also have an impact on the colour of the solvent. Treated solvent is expected to be lighter than untreated degraded solvent. The change in colour can be quantified with a UV-Vis spectrometer. Finally, the ammonia levels from the top of the absorber will be monitored during the campaign. Ammonia is one of the volatile end products resulting from oxidative degradation of amines which can be monitored easily and the increase in concentration is related to an increase in solvent degradation. If the activated carbon column is able to decrease degradation it is expected that the ammonia emissions will be lower than the situation when the column is not online.

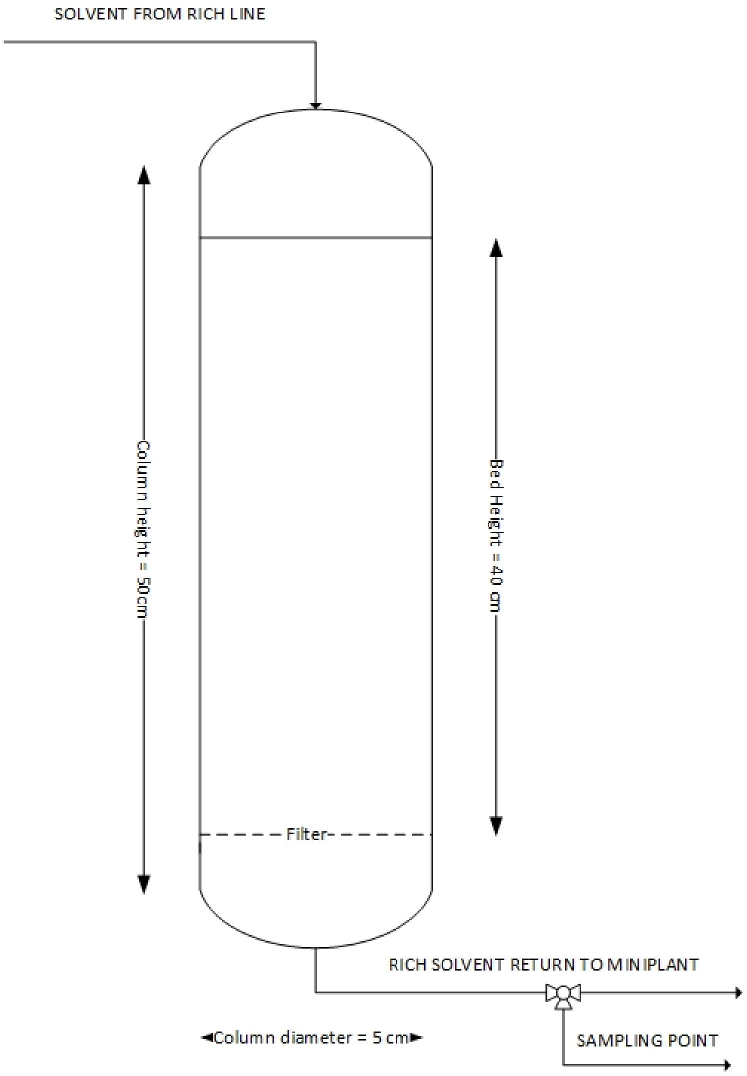

Figure 1 - Activated carbon column schematic

Laboratory tests will also be carried out to determine the breakthrough time of the selected carbon and estimate the lifetime of the activated carbon before it needs to be replaced. This will be done by circulating degraded solvent from the Miniplant over the column over time. Throughout this circulation regular samples will be taken and the absorbance of these samples will be measured. It is expected that when the carbon is saturated, the absorbance will stabilize and not reduce. These tests will be performed by TNO after some degraded solvent is available from the onsite testing in Ireland.

2.2 Selection of Activated Carbon

A commercial carbon has been selected for operation in the column shown above. Norit® GAC 830W from Cabot has been chosen as it is used extensively for removal of impurities such as organics and metals from water and other industrial process liquids. A series of laboratory tests were carried out at TNO with this carbon to test the extent of iron removal from water. Predetermined amounts of iron sulphate (Fe_2SO_4) were added to demineralized water and placed in a beaker with 1 g of the selected activated carbon. The amount of iron in the water was measured after 30 minutes and 60 minutes of contact with the carbon by using iron detection strips from Sigma Aldrich [17]. Table 1 shows that the carbon is capable of removing iron from demineralized water.

Table 1 – Iron removal from water using selected activated carbon

Sample	Initial concentration (mg/l)	Concentration at 30 min (mg/l)	Concentration at 60 min (mg/l)	Removal at 30 minutes (%)	Removal at 60 minutes (%)
1	10	2	0 – 2	80	>80
2	24	2	0 – 2	90	>90
3	101	25	10	75	90

The high removal of iron from water indicates that the carbon is capable of adsorbing metals. This is a desirable result, which if replicated in amines can lead to a mitigation of the effect of metals on amine degradation.

3 Dissolved Oxygen Removal

Mitigation of oxidative degradation can be achieved through the removal of dissolved oxygen from the capture solvent. This removal can be achieved through the introduction of oxygen scavengers, by nitrogen sparging or using membranes. In previous projects, TNO has patented and developed DORA (**D**issolved **O**xygen **R**emoval **A**pparatus), which is an online, non-invasive membrane-based solvent management tool. DORA employs membranes that remove dissolved oxygen from the aqueous amines leading to a reduction in oxidative degradation. The driving force for oxygen removal is provided by a sweeping gas on the shell side in combination with vacuum [13]. The use of DORA allows for the removal of oxygen from the solvent without addition of chemicals thereby avoiding side effects like foaming and more undesirable reactions [18], [19]. To date, DORA has been tested using commercially available porous membranes and a dense layer membrane fabricated by NTNU [13].

TNO has tested DORA in different configurations up to TRL 6 with a commercial porous membrane. These tests were carried out with artificial and real flue gases in combination with TNO’s Miniplant using 30wt% monoethanolamine (MEA). For one of these testing campaigns, the Miniplant was transported to an industrial facility in Rotterdam. A diesel generator was used as the flue gas source. CO_2 capture was done with 30wt% MEA and DORA was integrated in the Miniplant after the absorber sump. During the course of this campaign the DORA was tuned on and off to assess the impact of oxygen removal by the membrane. These tests demonstrated that the DORA was effective in removing more than 90% of the dissolved oxygen from the solvent and controlling the amount of degradation products like formate, acetate and oxalate [20]. Figure 2 shows the accumulation of formic acid in the solvent. The figure clearly shows that when DORA is online (indicated by the yellow box) that the formic acid levels stabilises followed by a sharp increase in the formic acid levels when DORA is offline.

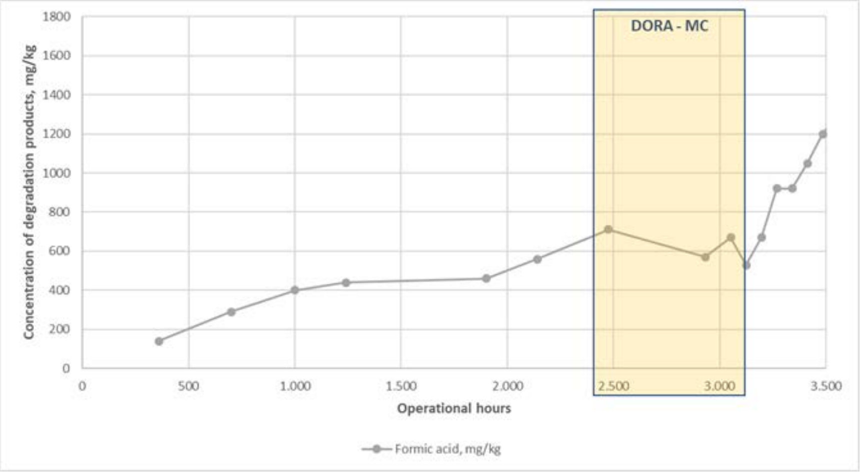

Figure 2 – Effect of DORA on accumulation of formic acid [20]

The campaign at the industrial facility in Rotterdam demonstrated that DORA is an effective solvent management technique that can control the accumulation of formate, acetate and oxalate in the solvent. However, towards the end of the aforementioned campaign it was observed that the membrane efficiency reduced overtime. This was attributed to amine leakages through the porous membrane. The resulting pore wetting led to damage and as a result the membrane was no longer effective. To mitigate the effect of pore wetting, TNO tested a dense layer membrane developed by NTNU [21] to remove oxygen from CO_2 capture solvents. These membranes have a polymeric coating on porous support. The polymeric coating prevents amine leakages, prolonging membrane lifetime. To achieve maximum oxygen removal from the solvent, the entire solvent flow of a capture plant should be treated. For the miniplant this translates to a maximum solvent flowrate of 20 l/h. The dense layer membrane from NTNU is a small membrane that cannot treat this flow. As a result, a commercial porous membrane will be used for oxygen removal in combination with the Miniplant at Irving Refinery.

A series of laboratory tests were also carried out with 30wt% MEA and the dense layer membrane, from NTNU, in TNO's Oxygen Depletion Installation (ODIN) to determine the optimised conditions for operating DORA. These tests were carried out under different operating conditions – varying sweep gases and flows, enhanced driving force with vacuum, and several CO_2 loadings.

3.1 Description of Membrane and Laboratory Setup

3.1.1 Description of Membranes

The porous membrane used in aforementioned tests is a commercially available module from 3M. The membrane contactor module from Liqui-Cel^{TM} SP Series (2.5 x 8 extra-flow model), consists of polypropylene hollow fibres with 25% porosity [22]. This membrane will be used for oxygen removal during the Miniplant campaign at Irving refinery.

The dense layer membrane was originally developed by Ansaloni et al. at NTNU as a membrane contactor for amine-based CO_2 capture [21]. The membrane developed used a porous polypropylene (PP) support (Celgard® 2400). This support has a thickness of 25 µm and porosity of 41% [23]. Fluorinated polymers were chosen for the dense layer coating since they provide chemical stability towards various amines and also provide high CO_2 selectivity over the amines [24]. The coating was carried by dip coating and a coating thickness of 1.7 ± 0.3 µm was achieved [21]. The dense layer is placed in contact with the amine solvent flowing on the shell side of the membrane and the sweep gas flows counter currently on the tube side. The total interfacial area of this membrane is 8.1cm^2. The membrane can be seen in Figure 3.

Figure 3 - Dense layer membrane fabricated for oxygen removal

3.1.2 Description of Laboratory Setup

The dense layer membrane shown above was tested with TNO’s **O**xygen **D**epletion **In**stallation (ODIN). This setup consists of two closed jacketed vessels of volume 0.67 litres each. The vessels are connected to a water bath, that allows for precise temperature control. The temperature of the solvent is measured with a type K thermocouple. The solvent is stirred continuously with a magnetic stirrer. The oxygen decay in the solvent is measured using an oxygen sensor from Endress+Hauser (Memosens COS81D). This sensor is capable of measuring oxygen in the range of 0.004mg/l to 30 mg/l. The sensor accuracy is 0.5 mg/l in the operating ranges used for this work [25]. This sensor has been validated against two other sensors - VWR pHenomenal® OX-4100 galvanic sensor and a HI-5421 dissolved oxygen and BOD meter from Hanna Instruments. In addition to this validation, the sensor has also been validated against literature and exhibits good agreement with all three validation methods [19]. A schematic of the setup is shown in Figure 4.

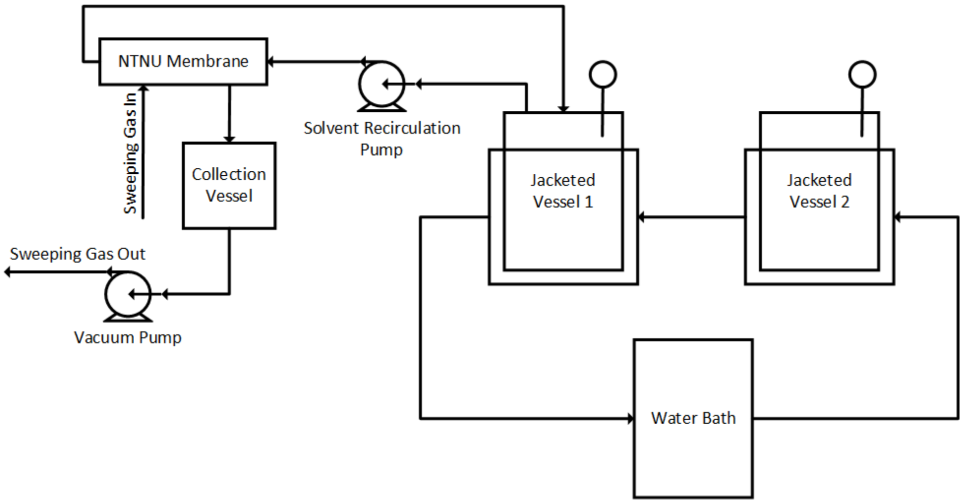

Figure 4 - Scheme of TNO's Oxygen Depletion Installation (ODIN) with DORA

DORA can be attached to either jacketed vessel. The solvent is recirculated over the membrane on the shell side with the help of a pump. Sweeping gas is introduced to the membrane on the tube side and flows counter-currently to the solvent. The gas outlet can be connected to a vacuum pump in order to increase driving force. A collection vessel is placed between the membrane and vacuum pump to collect any solvent that may leak through the membrane. Figure 5 shows the setup.

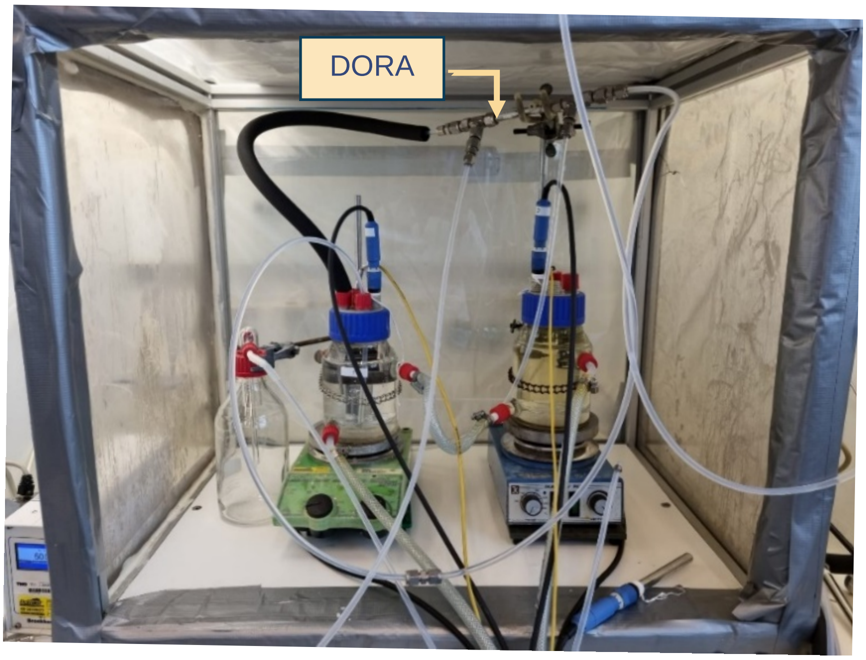

Figure 5 - TNO's Oxygen Depletion Installation (ODIN) with DORA

3.2 Experimental Methodology

To determine the extent of oxygen removal through DORA, tests with and without the membrane were performed in the ODIN. The solvent is either tested without CO_2 loading or it is loaded with a predetermined amount of CO_2. The CO_2 loading is measured using an ATR-FTIR. Tests are carried out without CO_2 loading and with CO_2 loading to gain an understanding of reaction kinetics and identify the impact of CO_2 loading on the rate of oxygen decay. The loaded solvent is charged to the vessel and allowed to reach the selected operating temperature. After reaching the desired temperature, the solvent is loaded with oxygen using pure oxygen. Tests can also be carried out with lower partial pressures of oxygen. However, since it is difficult to observe the impact of DORA at lower partial pressures, experiments were carried out with pure oxygen. When the oxygen concentration stabilizes, the vessels are filled to the top, so that no gas head space is left, and the oxygen sensor is introduced to the vessel. Special attention must be paid to potential trapping of bubbles on the sensor tip. To avoid measurement errors caused by such bubbles, the sensor is taken out and reinserted in the vessel. The vessel is sealed with a plug. The oxygen is then allowed to decay in the solvent over time. These experiments provide a baseline of oxygen consumption against which the performance of DORA can be assessed. The entire ODIN setup is placed inside a glove box purged with nitrogen to avoid any potential leak of oxygen into the vessel.

In the second set of experiments, the dense layer membrane (DORA) was attached to the vessel. The solvent is circulated over the vessel by means of a pump. The selected sweep gas flows counter currently on the porous side of the membrane. In these tests, the oxygen is removed from the solvent by means of the membrane but is also consumed via the oxidative degradation reactions. Therefore, the tests without the membrane (oxygen decay only due to reaction) serve as zero tests and allow us to assess the effect of the membrane in isolation. In some tests, the gas outlet of the membrane was also connected to a vacuum pump to enhance the driving force and reduce the flow of the sweep gas. All tests were performed in duplicates to assess repeatability.

3.3 DORA tests with 30wt% Monoethanolamine

Laboratory tests were carried out with 30wt% MEA since it is a benchmark solvent. Baseline tests were carried out to measure the decay of oxygen in 30wt% MEA at different CO_2 loadings and temperatures to reflect absorber conditions. DORA tests were then carried out at the same CO_2 loadings and temperatures to assess the extent of oxygen removal. This is important due to the fact that the DORA will be placed after the sump of the absorber.

3.3.1 DORA Tests with Varying Sweep Gas Flow Rates

Once baseline experiments were carried out, the ODIN was connected to the dense layer membrane. 30wt% MEA with no CO_2 loading was circulated over the membrane on the shell side. Nitrogen was used as a sweep gas and flowed counter-currently on the tube side. The nitrogen flow was varied from 25 Nl/h to 100 Nl/h. An overview of the experimental conditions used for these experiments is provided in Table 2.

Table 2 - Overview of experimental conditions for varying sweep gas flow rates

Experiment ID	Sweeping Gas	Gas Flow Rate (Nl/h)	Gas Outlet Pressure (bara)	CO_2 Loading (molCO_2/molMEA)	Temperature (°C)
1	-	-	-	0	40
2	N_2	100	1.01	0	40
3	N_2	50	1.01	0	40
4	N_2	25	1.01	0	40

Figure 6 shows that the gas flow rate does not have a significant impact on the amount of oxygen removed or the rate of removal. The liquid flow rate was fixed at 3 l/h as determined by previous work done at TNO [13].

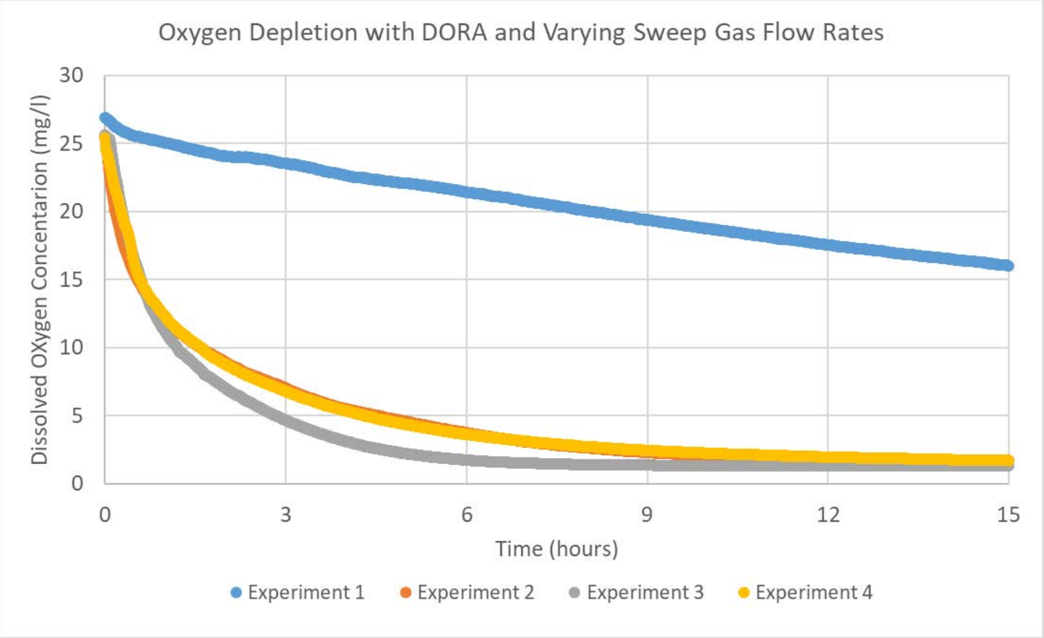

Figure 6 – Oxygen depletion in 30wt% MEA with DORA and varying sweep gas flow rates

3.3.2 DORA Tests with Vacuum

To provide driving force for oxygen removal a sweep gas is used. However, the amount of sweep gas needed for this removal can be a limiting factor to large scale implementation of this technology, therefore, the optimum value is essential to further upscale the technology. This driving force can also be provided by increasing the pressure difference across the membrane. To provide this driving force while reducing the amount of sweeping gas used, the gas outlet was attached to a vacuum pump which allowed to reduce the flow of nitrogen. Laboratory tests carried out with vacuum show that a sweep gas flow rate of 1 Nl/h with outlet pressure of 850 mbar provided the same removal as 100 Nl/h of sweep gas without vacuum. This can be seen in Figure 7 with the associated operating conditions in Table 3.

Table 3 - Overview of experimental conditions for DORA with vacuum

Experiment ID	Sweeping Gas	Gas Flow Rate (Nl/h)	Gas Outlet Pressure (bara)	CO_2 Loading ($molCO_2/molMEA$)	Temperature (°C)
1	-	-	-	0	40
2	N_2	100	1.01	0	40
5	N_2	1	0.85	0	40

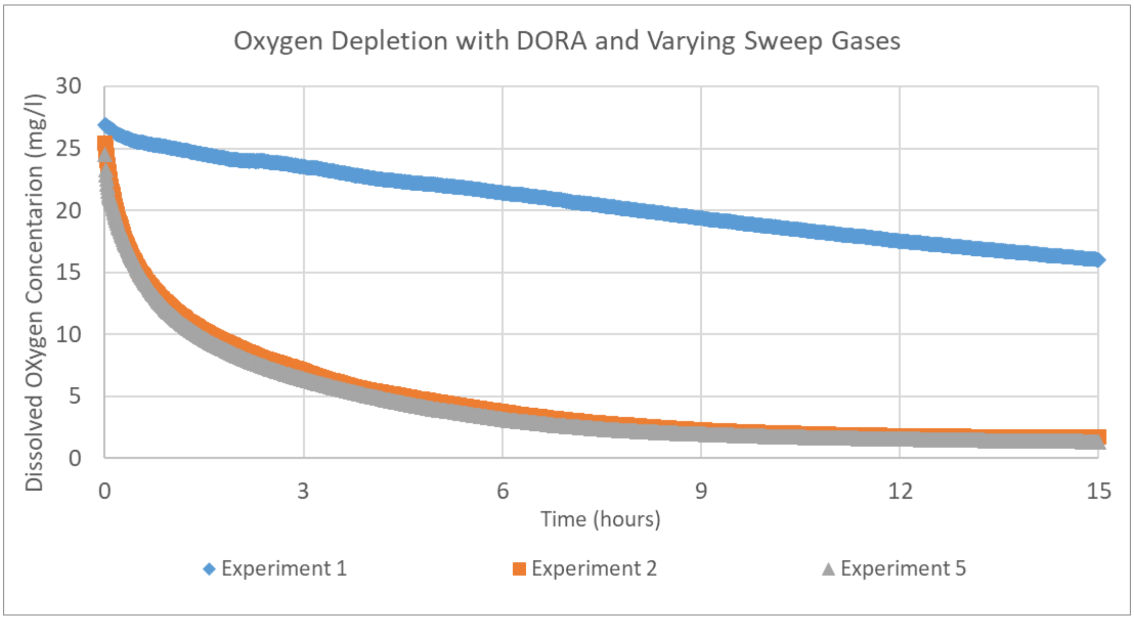

Figure 7 - Oxygen depletion in 30wt% MEA with DORA and vacuum

3.3.3 DORA Tests with Loaded Solvent

DORA will be integrated with the Miniplant in the rich solvent line after the absorber sump. To test the effectiveness of DORA in a realistic environment, tests were carried out with loaded solvents. The rate of oxygen decay in loaded solvents is much faster than that in unloaded solvents. Tests carried out with DORA indicate that the membrane is still capable of removing dissolved oxygen from loaded solvents in spite of the accelerated oxygen consumption. The conditions used for these tests have been summarized in Table 4.

Table 4 - Overview of experimental conditions for DORA with loaded solvent

Experiment ID	Sweeping Gas	Gas Flow Rate (Nl/h)	Gas Outlet Pressure (bara)	CO_2 Loading (molCO_2/molMEA)	Temperature (°C)
6	-	-	-	0.27	40
7	-	-	-	0.5	40
8	N_2	50	0.6	0.27	40
9	N_2	50	0.6	0.5	40

Figure 8 shows the oxygen depletion in a 30wt% MEA solution with CO_2 loading of 0.27 molCO_2/molMEA at 40°C. Experiment 6 shows the oxygen decay in this solution without the use of the membrane and experiment 8 shows the oxygen removal with DORA attached to the system. Clearly, the rate of decay is increased with DORA and this is attributed to the removal of oxygen from the solvent through the membrane.

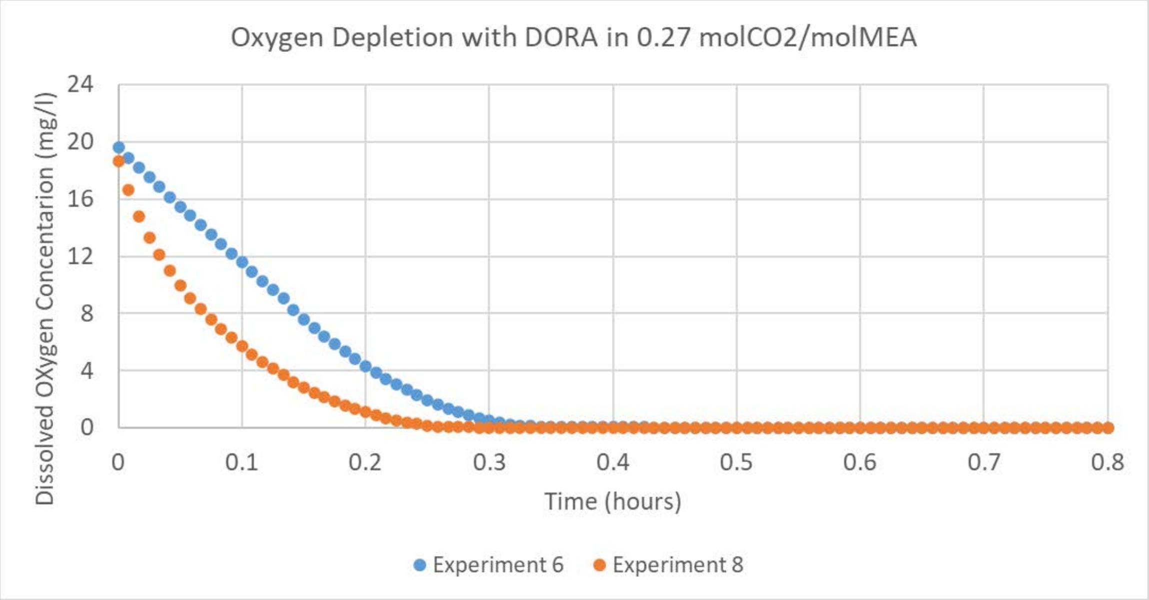

Figure 8 - Oxygen depletion in 30wt% MEA with 0.27 molCO$_2$/molMEA with and without DORA

Figure 9 shows the oxygen depletion in 30wt% MEA with a CO_2 loading of 0.5 molCO$_2$/molMEA. Experiment 7 shows the oxygen depletion without DORA and the effect of DORA can be seen in experiment 9. Removal rate is the highest at the beginning of the experiment. However, the rate seems to stagnate after 5 minutes. This indicates that further optimization of gas flow rates is required, and this can be achieved with increasing the driving force with deeper vacuum. This will be tested in the future.

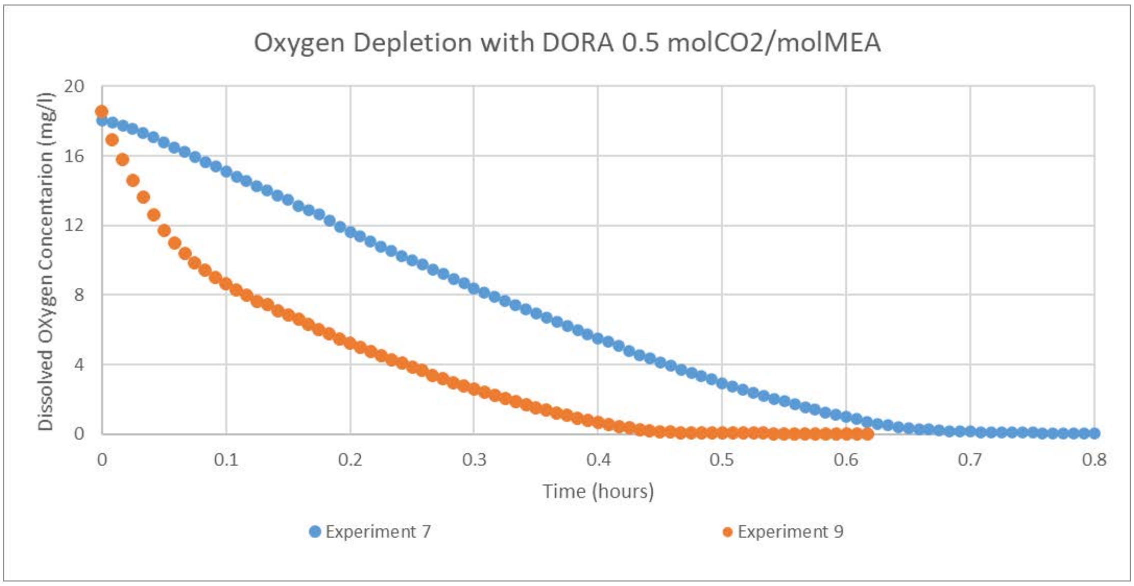

Figure 9 - Oxygen depletion in 30wt% MEA with 0.5 molCO$_2$/molMEA with and without DORA

3.4 Integration with the Miniplant

DORA will be tested with TNO’s Miniplant during the campaign at Irving refinery. The membrane will be placed in the rich line after the absorber sump. The entire rich stream will flow through the membrane. Since the dense layer membrane used for laboratory testing cannot handle the entire rich solvent flow, a larger commercial porous membrane will be used for testing. The miniplant will first be operated without DORA at Irving refinery. During this time, the plant operation and solvent quality will be monitored. When stable operation has been attained and the solvent has started degrading, DORA will be introduced to the plant. The impact of DORA on solvent degradation will be monitored in three ways:

- Monitoring ammonia emissions from the absorber. Since DORA removes dissolved oxygen from the solvent, the rate of oxidative degradation is expected to reduce. As a result, the amount of ammonia generated should also stabilise and not increase overtime. The online FTIR connected to the Miniplant will provide this data.
- Samples will be taken from the rich solvent regularly and analysed for degradation products. The concentration of degradation products should stop increasing in the presence of DORA.
- An online oxygen sensor will be installed to measure the oxygen level in the solvent after it passes through DORA. Baseline measurements will be carried out with the oxygen sensor to measure dissolved oxygen levels without DORA.

4 Solvent Reclaiming

Solvent reclaiming is a solvent management strategy aimed at recovery of amines from degraded solvents. Reclaiming can be done through various mechanisms – ion exchange, electrodialysis and thermal reclaiming. Within this project thermal reclaiming of degraded solvents will be investigated as a solvent management strategy.

4.1 Thermal Reclaiming

The thermal reclaiming process uses heat for purification of amines. Normally, thermal reclaiming involves mixing of degraded amine with NaOH or Na_2CO_3 to neutralize and release the amines that are in the conjugated acid form in HSS structures. This also leads to increased recovery of amines and lower solvent losses. Three main types of thermal reclaimers exist – classical thermal reclaimers that operate at atmospheric pressures or above; modern thermal reclaimers that operate at pressures below atmospheric; and molecular distillation reclaimers that operate at deep vacuum. Thermal reclaiming can be carried out either in a batch, semi-continuous or continuous mode. Classical thermal reclaiming of amines is carried out at temperatures higher than those encountered in the stripper. For 30wt% MEA, reclaiming has been carried out at temperatures around 130°C [8]. However, long exposure to higher temperatures can lead to increased degradation of solvents. Therefore, alternative designs make use of vacuum to be able to recover the amine(s) at lower temperature.

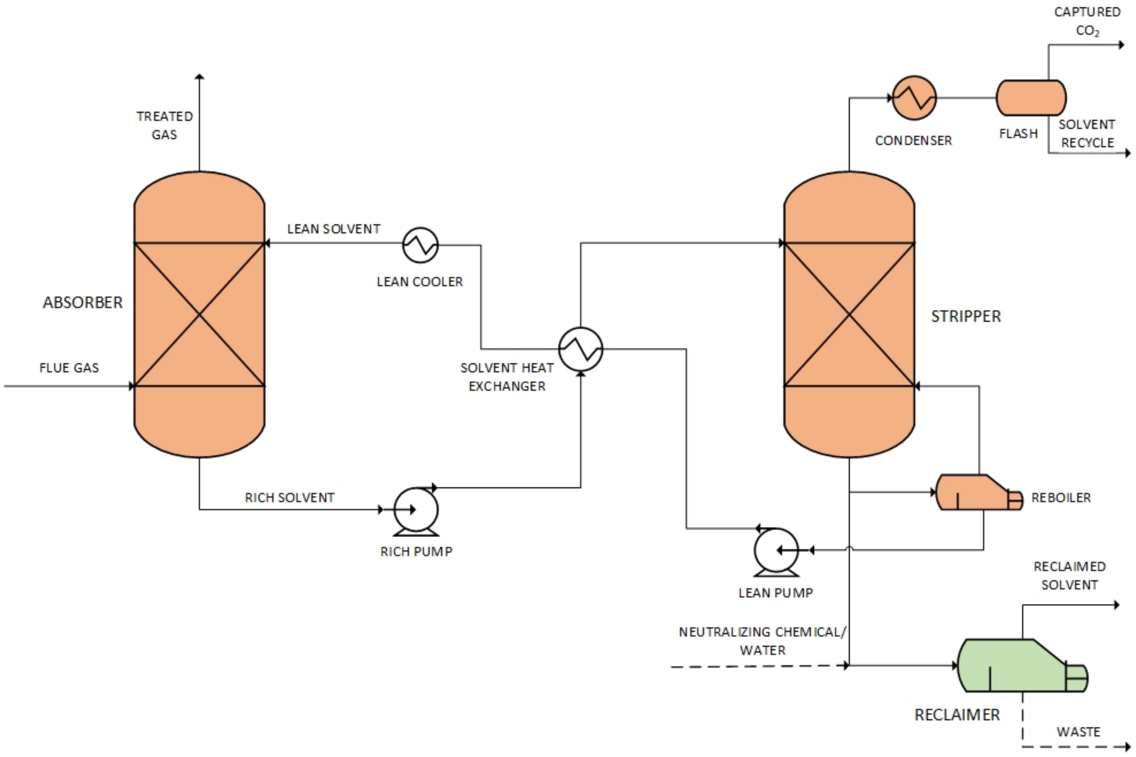

Figure 10 - Classical thermal reclaimer with an amine-based CO_2 capture plant

Figure 10 shows a scheme in which a classical thermal reclaimer is used to treat a slip stream from an amine-based CO_2 capture plant. Neutralization agents are added to the reclaimer and the reclaimed solvent can be either recycled to the plant (as a vapor) or condensed, collected and fed to the plant when necessary. The bottom stream from the reclaimer contains impurities like degradation products and metals. This waste is usually classified as hazardous waste.

Thermal reclaiming has several advantages over other strategies. Reclaiming is an economical strategy when the contamination levels are medium to high [10]. The waste stream produced by the reclaiming operation is much smaller than that produced by solvent replacement. This minimizes overall waste handling and associated costs. The consumption of chemicals and water is low.

The key limitations of thermal reclaiming include high energy consumption and production of hazardous waste. If not sized and operated properly, thermal reclaimers can result in high amine losses. Additionally, thermal reclaimers are not economical for purification of solvents when the amount of impurities is low.

4.2 Thermal Reclaiming of Blends

Thermal reclaiming has been demonstrated and reported for solvent systems contain only one amine and so the reclaiming can be carried out at a single temperature (e.g. 130°C for MEA). However, reclaiming of blends will require a change in strategy since the different components in the blend will be recovered at different temperatures. This can be realised by using different vessels for different amines or by application of different conditions in the same vessel. These options will be investigated with degraded HS-3 in TNO laboratories. The aim is to design a method and equipment for reclaiming amines from degraded blends and determine the recovery and energy demand associated with such a method. These tests will be carried out when degraded solvent is available from the Miniplant campaign at Irving refinery.

5 Conclusions

Degradation of amines used for post combustion CO_2 capture is a major challenge that leads to a wide variety of issues that negatively impact process economics, plant operation and may also adversely impact environmental effects of the process. Solvent management techniques can mitigate the impacts of solvent degradation. These techniques can either be proactive or reactive.

Reactive strategies such as solvent changeover, 'bleed and feed', reclaiming are applied after the solvent has degraded to a certain acceptable threshold. On the other hand, proactive strategies are applied online and treat the solvent during operation of the plant. These techniques include mechanical filtration, adsorption with activated carbon, oxygen removal through nitrogen sparging or membranes.

Within REALISE, three solvent management techniques have been selected for investigation – oxygen removal through membranes, adsorption with activated carbon and thermal reclaiming. While the first two strategies will be tested online, thermal reclaiming will be carried out offline at TNO's laboratories.

Activated carbon can be used for removal of undesirable products and impurities from amines. A column with activated column will be placed in the rich line between the absorber sump and solvent heat exchanger. A column was designed to treat 10% of the total solvent flow in the Miniplant. The activate carbon column will be integrated with the Miniplant at Irving refinery after stable operation has been achieved and the solvent has attained an agreed upon degradation threshold. A commercial activated carbon will be used for this campaign. The impact of the activated carbon column will be evaluated on the basis of amount of degradation compounds and impurities in samples, through UV-Vis spectroscopy and monitoring of ammonia levels.

Dissolved oxygen removal from amines can mitigate the extent of oxidative degradation of amines. TNO has developed and patented the **D**issolved **O**xygen **R**emoval **A**pparatus (DORA) that removes dissolved oxygen from amines through membranes. TNO has tested commercial porous membranes for this application at TRL6 at industrially relevant conditions. It was seen that DORA is capable of removing upto 90% oxygen from the solvent. Test campaigns have also shown that while DORA is online, the level of degradation products ,such as formate, acetate and oxalate, in the solvent stabilises as opposed to a sharp increase that is seen in the absence of DORA. Commercially available porous membranes will be used for oxygen removal at Irving refinery. Like the activated carbon column, DORA will be introduced into the system when stable operation has been achieved and the solvent has reached the agreed upon threshold limit. The impact of DORA will be assessed on the basis of degradation products in solvent samples taken over time and the levels of ammonia emissions from the absorber.

Finally, at the end of the Miniplant campaign with HS-3 solvent, TNO will carry out thermal reclaiming. These tests will be carried out at TNO's laboratories and will be carried out in a setup designed for reclaiming of blends. The tests will be aimed at determination of optimum operating conditions, quantifying amine recoveries and energy demand.

The tests descried above will lead to generation of information and data that will be used for a techno-economic analysis. This will provide an indication of the costs associated with these techniques. The test campaigns will also provide information on the effectiveness of these technologies.

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