TECHNO-ECONOMIC PERFORMANCE OF DORA WITH MEA AND CESAR1

Tanya Srivastava[1*], Roberta V. Figueiredo[1], Tarjei Skaar[1], Niels Warning[1], Paul Gravesteijn[1], Juliana Monteiro[1], Peter van Os[1], Earl Goetheer[1]

[1] TNO, Leeghwaterstraat 46, 2628CA, Delft, Netherlands

* Corresponding author e-mail: tanya.srivastava@tno.nl

Abstract

Solvent degradation is one of the major challenges to widespread implementation of post combustion CO_2 capture (PCCC) using amine based capture solvents. The presence of oxygen in the flue gas leads to degradation and formation of heat stable salts (HSS). Oxidative degradation can be limited by removal of dissolved oxygen from the capture solvent. TNO has developed DORA (**D**issolved **O**xygen **R**emoval **A**pparatus) as a counter measure for oxidative degradation using membranes. DORA was tested in an industrial environment at PlantOne in Rotterdam with TNO's mobile CO_2 capture plant using 30 wt% MEA. The experimental campaign showed that DORA was effective in oxygen removal and stabilizing the amount of degradation products in the solvent, However, during this campaign it was also observed that porous hollow fiber membranes are not suitable for long-term use. The membrane was damaged due to pore wetting and amine leakages towards the end of the campaign. A more advanced membrane developed by NTNU was tested at TNO laboratories and it was observed that this membrane has a dissolved oxygen removal efficiency greater than 90% for 30wt% MEA. Similar tests were also performed with CESAR1 to demonstrate the solvent independent nature of the technology. To quantify the impact of DORA a techno economic assessment was carried out for 30 wt% MEA and CESAR1. The amount of heat stable salts formed when operating a PCCC plant with DORA was calculated using a degradation network model. It was estimated that the amount of heat stable salts formed would be reduced by 86%. This decrease also leads to a reduction in the number of thermal reclaiming cycles needed to maintain solvent quality. The costs of thermal reclaiming with and without DORA have been estimated in this work.

Keywords: *Oxygen removal, oxidative degradation, CO_2 capture, solvent management*

1. Introduction

The acceleration of CO_2 capture process implementation is critical to achieving climate goals. Post combustion CO_2 capture using absorption technology has been widely investigated. Absorption technology using aqueous amines, has been demonstrated at industrial scale and has shown promising results [1],[2].

However, solvent degradation in absorption based capture plants poses a challenge to widespread implementation. Some of these challenges include corrosivity, waste management and emissions. Amine degradation by thermal and oxidative mechanisms leads to increased operational costs.

Oxygen present in the flue gas dissolves when in contact with the solvent and leads to several irreversible reactions. Therefore, removal of dissolved oxygen from the solvent is a possible strategy to overcome oxidative degradation. This can be done by several approaches such as use of inhibitors (oxygen scavengers), or by promoting the oxygen separation (by nitrogen sparging, or using membranes) [3].

1.1 DORA as a tool for solvent management

DORA (**D**issolved **O**xygen **R**emoval **A**pparatus) is a membrane based technology developed by TNO as a mitigation strategy for oxidative degradation. The solvent passes through the DORA (an online tool) and the oxygen is removed by means of a sweeping gas (such as nitrogen or CO_2). This prevents direct contact of the solvent with other chemicals or gases avoiding undesirable effects such as side reactions and foaming [4], [5]. A commercially available porous membrane and a dense layer membrane fabricated by NTNU [6] were previously tested for dissolved oxygen removal from MEA.

Demonstrating the solvent independent nature of DORA was achieved with experiments using CESAR1. These experiments were used to perform a techno-economic evaluation to determine impact and relevance of DORA for CO_2 capture plants at different scales.

2. Experimental work

2.1 Tests with porous membrane

As part of ERA-ACT ALIGN and NCCS projects, previous tests were done at TNO using the DORA in combination with TNO's capture plant (Miniplant). The membrane used was a commercially available porous membrane from Liqui-Cel® which was connected in a bypass configuration after the sump of the absorber allowing the flexibility to operate inline or in the bypass mode.

The campaigns consisted of operation with and without the DORA illustrating its impact on solvent degradation. During two months, the Miniplant was operational and the gas outlet of the absorber was monitored. Ammonia emissions were used as an indication of degradation since it is one of the major degradation compounds that is formed in the process. Figure 1 shows that during the operation with the DORA the ammonia levels were constant and controlled. In contrast, when the membrane was not in operation, the ammonia levels increased and showed significant variations. The same behavior was observed during the second operation of the DORA. The gas outlet of the DORA was also monitored to ensure that the decrease in ammonia levels was not due to ammonia escaping through the membrane.

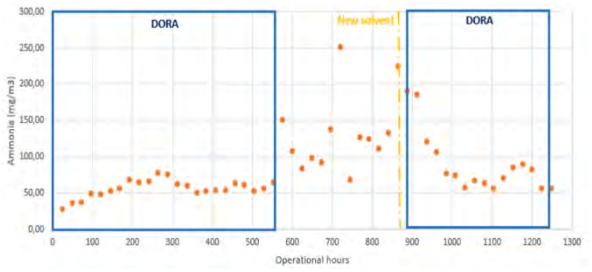

Figure 1 - Miniplant operation with and without the DORA

The previous experiments were carried out with artificial flue gas at TNO, however, a follow-up campaign was performed with the Miniplant at PlantOne (facility in Rotterdam that provided real flue gas) to characterize the DORA operation in relevant conditions.

The Miniplant was operated for 9 months and the DORA was once more coupled to the system after the absorber sump and was online at different times. In these experiments, it was decided to monitor the accumulation of oxidative degradation products in the liquid phase. The concentration of acetate, formate and oxalate in the liquid were analyzed by an external lab.

Figure 2 shows the results of the formic acid analysis and the periods in which the DORA was operated. The same is shown in Figure 3 for acetic acid and oxalate. Although the operation of DORA was not continuous, a clear correlation was observed between the operation and the stabilization degradation products and the control of degradation of MEA.

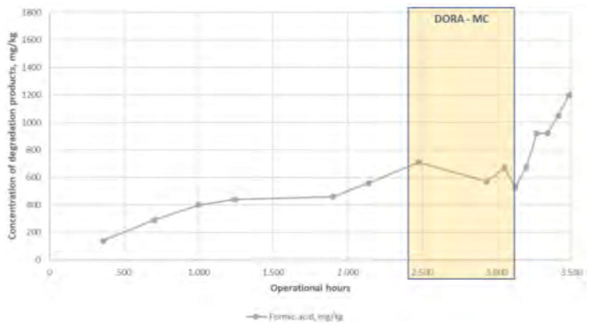

Figure 2 - DORA operation integrated in the Miniplant, formate content (expressed as formic acid). The yellow rectangle indicates the period in which DORA was operational.

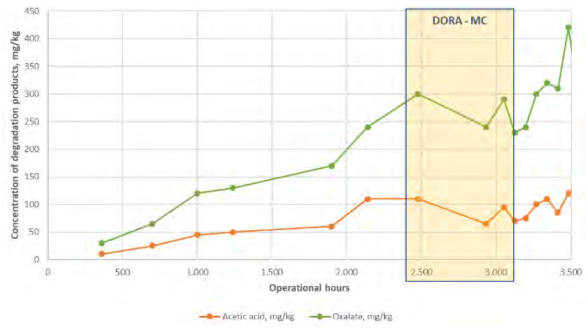

Figure 3 - DORA operation integrated in the Miniplant, acetate (expressed as acetic acid) and oxalate contents

The operation of DORA at PlantOne showed promising results for the DORA technology, however, it gave insights on the sensitivity of the porous membrane. Leakages and wetting of the pores were observed which lead to a decay in the oxygen removal efficiency towards the end of the campaign.

To overcome these issues an advanced membrane developed by NTNU was tested at TNO and compared with the damaged porous membrane Figure 4.

The tests show that oxygen removal rate with the NTNU membrane was acceptable, whereas the damaged porous membrane was completely inefficient. For this reason, further tests were done with the NTNU membrane at TNO setup ODIN (**O**xygen **D**epletion **In**stallation) which are shown in Section 2.2

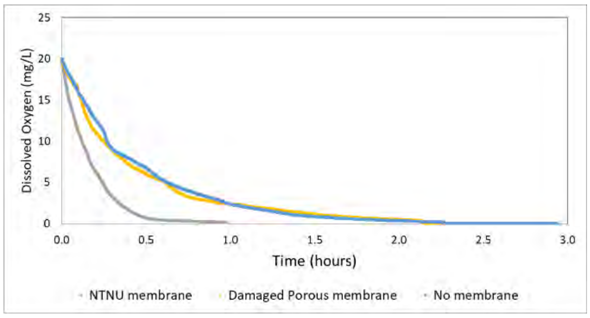

Figure 4 - Oxygen removal/degradation rates of the NTNU membrane, damaged Liqui-Cel® membrane and the set-up with no membrane

2.2 Tests with the dense layer membrane

Oxygen depletion tests without a membrane were done at TNO to characterize the behavior and performance of the NTNU membrane for the removal of oxygen. These tests were done in the ODIN setup of TNO (Figure 5), using MEA and an oxygen sensor from Endress+Hauser model COS81D-11L5/0 to measure the dissolved oxygen activity during the tests. The sensor used is an optical sensor with a membrane on the top, that when in contact with the liquid, allows the oxygen to permeate through and the activity to be measured [5].

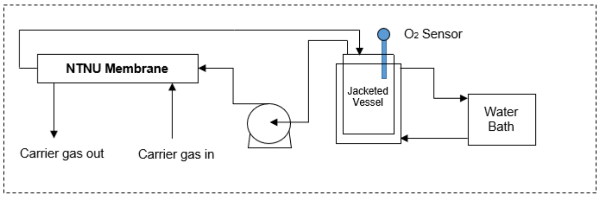

Figure 5 - Schematic of laboratorial setup for dense membrane tests (ODIN)

A set of tests was performed to check the influence of liquid and gas flow rates, temperature and CO_2 loading. Relative to the liquid flow, the liquid mass transfer resistance was observed to be the dominant factor meaning that, although the oxygen removal increases with higher flows, the increase is not proportional to the increase in the liquid flow rate. The trend for the gas flow experiments was similar, in addition to the fact that the flow rate increase is only significant until a "critical flow rate value" after which the removal rate is quite stable.

Varying the temperature of the liquid showed that higher temperatures lead to a faster depletion of oxygen, partly due to the lower solubility of gases at higher temperatures and also due to increased consumption of oxygen through oxidative degradation mechanisms, Figure 6.

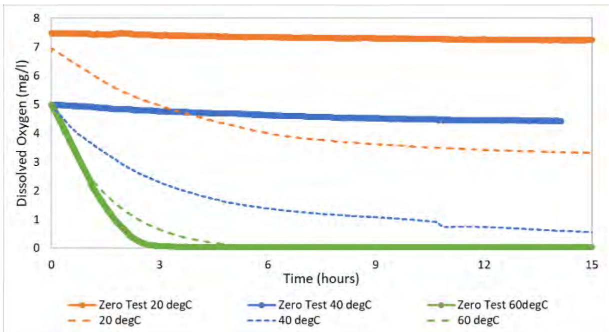

Figure 6 - The effect of temperature on oxygen removal rate. In these tests, a liquid circulation rate of 4.5 l/h is used, and the nitrogen flow is 100 l/h.

Investigating the effect of CO_2 loading on oxygen removal and consumption rate was also crucial as it was expected that the correlation between the two could be quite strong. The oxygen decay was much faster for higher loadings and pure oxygen was used instead of air to make sure the values would not get under the lower detection limit of the oxygen sensor. It was observed that, at 0.2 mol CO_2 / mol MEA, the complete consumption of oxygen took place in about 25 minutes. At rich conditions, and at typical flue gas oxygen content (therefore lower initial dissolved oxygen concentration), it is likely that the oxygen is totally consumed within the absorber sump (typical residence time 10-15 minutes), Figure 7.

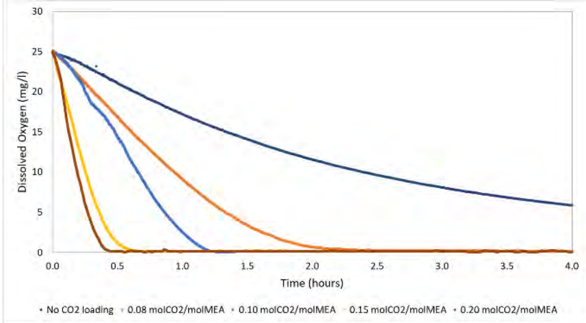

Figure 7 - The effect of CO_2 loading (in $molCO_2/molMEA$) on oxygen removal rates

The tests were key for the development of a model for the DORA to characterize the mass transfer of oxygen through the membrane.

2.3 Solvent Independent Nature of DORA

DORA has been developed as a solvent independent tool to reduce oxidative degradation of amines. To demonstrate this independence, DORA was tested with CESAR1, a second generation solvent blend of 2-Amino-2-methyl-1-propanol (AMP) and Piperazine (PZ).

First, tests without a membrane were carried out in the Oxygen Depletion Installation, ODIN (Figure 5). The purpose of these tests was to estimate the extent of oxygen consumption in CESAR1 over time. These tests were followed by experiments with NTNU's dense layer membrane described in the previous section. For both tests – without and with membrane, the solvent was loaded with air at 40°C. A liquid circulation rate of 3 l/h and carrier gas (N_2) flow rate of 75 l/h was used for these tests. As shown in Figure 8, it was observed that DORA is capable of removing more than 70% of dissolved oxygen from CESAR1.

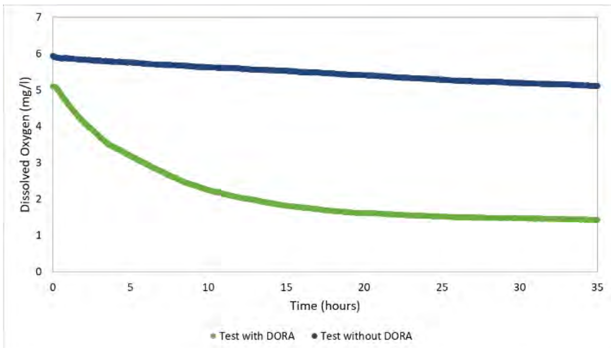

Figure 8 - Oxygen removal from CESAR1: tests with and without DORA

3. Techno-economic evaluation of DORA

A techno-economic evaluation of DORA was carried out to evaluate the impact of DORA for large scale CO_2 capture plants. Thermal reclaiming is one of the most advanced solvent management techniques. However, the process is energy intensive. The cost associated with thermal reclaiming can be reduced by means of heat integration [7]. This cost can also be reduced significantly by overall reduction of oxidative degradation using DORA.

3.1 Impact of DORA on oxidative degradation

In order to estimate the impact of DORA, the extent of oxygen consumption due to oxidative degradation was estimated with a degradation network model (DNM). This model was developed to quantify the consumption of oxygen under different operation conditions and was developed by TNO during ALIGN CCUS [8].

The oxidative degradation of capture solvents is dependent on various plant specific factors like residence times and temperatures in various units (absorber, absorber sump, piping, cross heat exchanger), quality of the flue gas and plant operation.

In order to develop an effective solvent management strategy, it is essential to understand where the most amount of solvent is degraded. From the DNM it was concluded that majority of the oxygen consumption occurs in the absorber sump. Thus, removing dissolved oxygen from the solvent before it enters the sump will be an effective strategy to reduce the extent of oxidative degradation. Integration of DORA in the capture plant before the sump will remove the oxygen and prevent the formation of degradation products.

The DNM was validated using data from the 18-month campaign with MEA conducted at the CO_2 capture pilot at Niederaussem in Germany [9]. The DNM was used to calculate the amount of formate, acetate and oxalate formed and was compared with results from sample analysis. From Figure 9, it is clear that the DNM can predict the formation of degradation products well up to 200 days. After 200 days, degradation of MEA enters and exponential regime and is not predicted well by the model.

Figure 9 - Validation of DNM with campaign data from RWE

The DNM was used to calculate the amount of formate, acetate and oxalate formed in the presence of DORA. A sensitivity analysis was carried out to determine the impact of DORA with different oxygen removal efficiencies in the linear regime of MEA degradation. It was found that with 50% oxygen removal the amount of formate, acetate and oxalate formed will reduce by 47%, followed by 75% for 80% oxygen removal and 86% in the case that 90% oxygen is removed. This analysis can be seen in Figure 10.

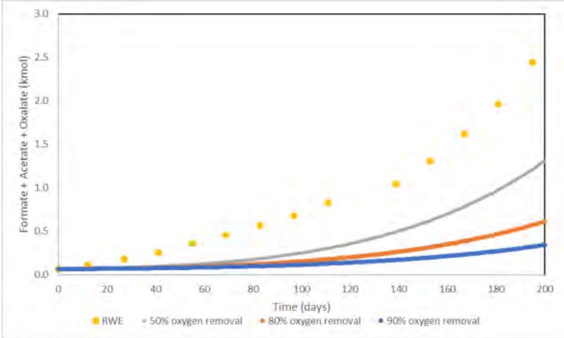

Figure 10 - Impact of DORA on formation of heat stable salts

3.2 Economic impact of DORA with 30wt% MEA

For stable operation of CO_2 capture plants, the total heat stable salt content of the solvent should be controlled. For MEA, the maximum solvent content as heat stable salt is normally controlled between 1% and 5%. Thermal reclaiming can be used to maintain heat stable salts within this range. An economic evaluation of the cost of thermal reclaiming was performed for the situation with and without DORA (base case), using the dense layer membrane. The analysis was carried out for a hypothetical CO_2 capture plant in The Netherlands with 90% capture, flue gas flowrate of 100 kt/h at 40°C and CO_2 concentration 8 vol%.

3.2.1 Base case with thermal reclaiming

Assuming thermal reclaiming can recover 90% of the degraded solvent, the costs associated with solvent replacement, reclaimer operation and waste handling for reclaimer sludge was calculated. The assumptions are listed in Table 1.

Table 1 - Assumptions for calculation of reclaiming costs for 30wt% MEA

Solvent cost (per kg)	€ 2,1 [10]
Reclaimer energy consumption (per kg HSS)	10 kWh [11]
Reclaimer waste disposal (per ton)	€ 375 [10]

The number of reclaiming cycles needed per year for maintaining a certain level of heat stable salts (formate, acetate, oxalate) in the plant was estimated from RWE campaign data (Table 2) .

Table 2 - Number of reclaiming cycles required

HSS content	1%	2%	3%	4%	5%
No. of cycles	6.6	3.5	2.5	2.2	2.1

To determine the cost of thermal reclaiming a range of electricity prices were assumed (Case1: 3 €cents/kWh; Case2 : 5 €cents/kWh; Case3: 7 €cents/kWh and Case4: 10 €cents/kWh). The normalized cost for thermal reclaiming for 30wt% MEA against overall cost per ton of CO_2 captured are shown in Figure 11.

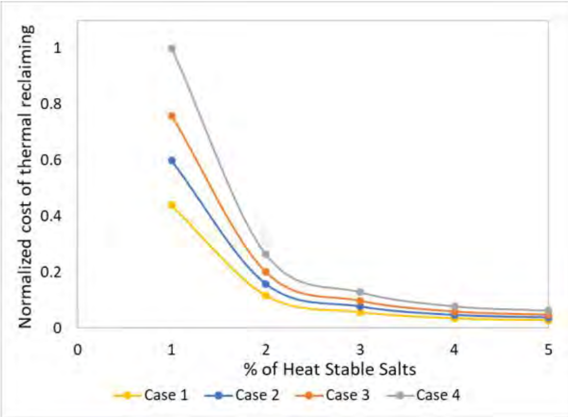

Figure 11 - Normalized cost of thermal reclaiming for 30wt% MEA

3.2.2 Thermal reclaiming with DORA

Integration of DORA in the CO_2 capture plant will lead to reduction of oxidative degradation. As a result, the amount of heat stable salts formed also reduces. In turn, the number of thermal reclaiming cycles needed to maintain a solvent quality with a pre-determined level of heat stable salts also decreases. The number of cycles necessary for maintaining these levels was determined using the DNM as described in the previous section (Table 3). It was assumed that DORA is integrated in the capture plant before the absorber sump can remove 90% of dissolved oxygen from the solvent.

Table 3 - Number of reclaiming cycles needed with DORA

HSS content	1%	2%	3%	4%	5%
No. of cycles	2.1	1.3	1.0	0.8	0.7

Figure 12 shows the impact of DORA on cost of thermal reclaiming for 30wt% MEA. The costs are reduced by 60% to 70% for the different cases.

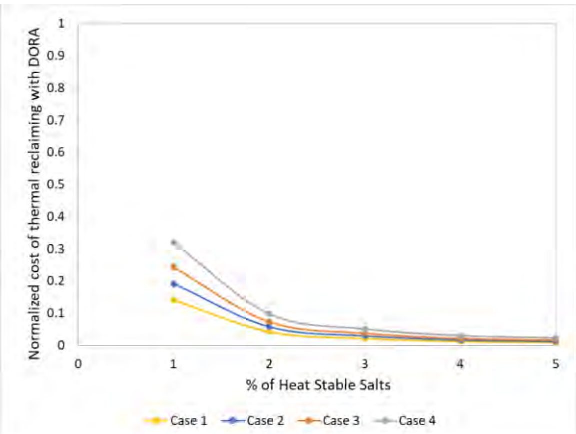

Figure 12 – Normalized cost of thermal reclaiming for 30wt% MEA with DORA

3.3 Economic impact of DORA with CESAR1

An analysis similar to the one described in section 3.2 was carried out for CESAR1. For this case, the following assumptions were taken into account (Table 4).

Table 4 - Assumptions for calculation of reclaiming costs for CESAR1

Solvent cost (per kg)	€ 8,1 [10]
Reclaimer energy consumption (per kg HSS)	8 kWh [11]
Reclaimer waste disposal (per ton)	€ 375 [10]

Figure 13 and Figure 14 show the normalized cost of thermal reclaiming for CESAR1 compared to 30wt% MEA. For this calculation it was assumed that the number of reclaiming cycles required per year is the same as 30 wt% MEA. Updated estimates of the reclaiming cycles will be made by development of the DNM for CESAR1. The estimated reduction of annual reclaiming costs with DORA is between 60% and 70% for the different cases.

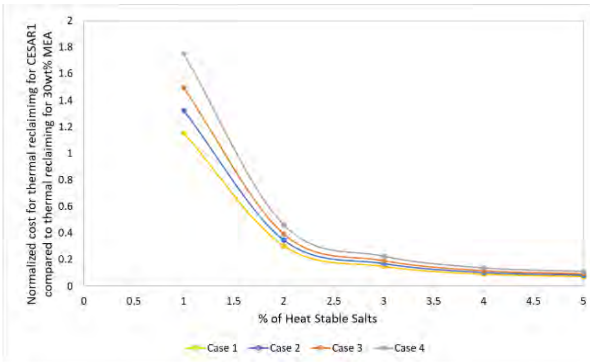

Figure 13 - Normalized costs for thermal reclaiming for CESAR1 compared with thermal reclaiming for 30wt% MEA

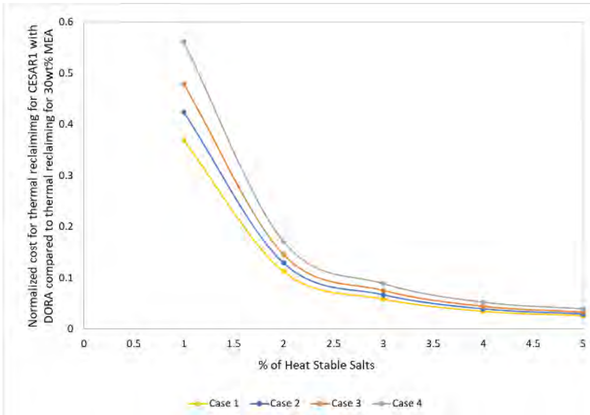

Figure 14 - Normalized costs for thermal reclaiming for CESAR1 with DORA compared to thermal reclaiming for 30wt% MEA

4. Conclusions and recommendations

Demonstration of DORA at PlantOne showed that it is capable of removing up to 90% dissolved oxygen from the solvent. This was achieved with a porous membrane that got damaged during operation due to pore wetting and leakages. Therefore, a better membrane is needed for this application. A more advanced membrane developed at NTNU was tested at laboratory scale with 30wt% MEA and CESAR1. Oxygen removal efficiencies of greater than 90% and 70% were observed for 30wt%MEA and CESAR1 respectively. For applications that require low oxygen in the CO_2 product, such as enhanced oil recovery and storage, DORA can be an effective tool to remove oxygen concentration from the captured CO_2.

A techno-economic evaluation of DORA with the advanced dense layer membrane was carried out to estimate its impact on solvent handling costs. DORA is capable of removing 86% of heat stable salts from 30wt% MEA. This reduction allows for a decrease of 60% to 70% in costs associated with thermal reclaiming. This reduction follows from the fact that fewer thermal reclaiming cycles are required to maintain solvent quality.

The economic analysis for CESAR1 indicated that the annual cost of reclaiming is expected to be higher due to increased solvent costs. However, this analysis was carried out assuming that the number of reclaiming cycles remains the same as 30wt% MEA. This estimate will be improved in future work by extending the degradation network model for CESAR1.

From the laboratory experiments it is evident that DORA is an effective solvent management tool. It assists in reduction of oxidative degradation and has the potential to reduce overall cost of CO_2 capture.

Acknowledgements

This publication has been produced with support from the NCCS Research Centre, performed under the Norwegian research program Centres for Environment-friendly Energy Research (FME). The authors acknowledge the following partners for their contributions: Aker Solutions, Ansaldo Energia, Baker Hughes, CoorsTek Membrane Sciences, EMGS, Equinor, Gassco, Krohne, Larvik Shipping, Lundin, Norcem, Norwegian Oil and Gas, Quad Geometrics, Total, Vår Energi, and the Research Council of Norway (257579/E20).

ACT ALIGN CCUS Project No 271501. This project has received funding from RVO (NL), FZJ/PtJ(DE), Gassnova(NO), UEFISCDI (RO), BEIS (UK) and is cofunded by the European Commission under the Horizon 2020 programme ACT, Grant Agreement No. 691712. www.alignccus.eu.

The LAUNCH project is funded through the ACT programme (Accelerating CCS Technologies, Horizon2020 Project No 294766). Financial contributions are made from: Netherlands Enterprise Agency (RVO), Netherlands; Bundesministerium für Wirtschaft und Energie (BMWi), Germany; Gassnova SF (GN), Norway; Department for Business, Energy & Industrial Strategy (BEIS) together with extra funding from NERC and EPSRC research councils, United Kingdom; US-Department of Energy (US-DOE), USA.

All funders are gratefully acknowledged.

References

[1] K. Stéphenne, "Start-up of world's first commercial post-combustion coal fired ccs project: Contribution of shell cansolv to saskpower boundary dam iccs project," Elsevier B.V., 2014.

[2] J. Jenkins, "Financing Mega-Scale Energy Projects: A Case Study of the Petra Nova Carbon Capture Project," 2015.

[3] P. T. Nielsen and G. T. Rochelle, "Effects of Catalysts, Inhibitors, and Contaminants on Piperazine Oxidation," *Energy Procedia*, vol. 114, pp. 1919–1929, 2017, doi: https://doi.org/10.1016/j.egypro.2017.03.1323.

[4] A. J. Sexton and G. T. Rochelle, "Catalysts and inhibitors for oxidative degradation of monoethanolamine," *Int. J. Greenh. Gas Control*, vol. 3, no. 6, pp. 704–711, 2009, doi: 10.1016/j.ijggc.2009.08.007.

[5] V. Buvik *et al.*, "Measurement and prediction of oxygen solubility in post-combustion CO_2 capture solvents," *Int. J. Greenh. Gas Control*, no. March, p. 103205, 2020, doi: 10.1016/j.ijggc.2020.103205.

[6] L. Ansaloni, R. Rennemo, H. K. Knuutila, and L. Deng, "Development of membrane contactors using volatile amine-based absorbents for CO_2 capture: Amine permeation through the membrane," *J. Memb. Sci.*, vol. 537, no. February, pp. 272–282, 2017, doi: 10.1016/j.memsci.2017.05.016.

[7] CO2CRC Limted, "Retrofitting an Australian brown coal power station with post-combustion capture," 2018.

[8] G. Wiechers *et al.*, "ALIGN-CCUS D1.2.6 Guidelines for effective solvent management," 2020.

[9] 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, no. September 2019, p. 102945, 2020, doi: 10.1016/j.ijggc.2019.102945.

[10] S. Garcia *et al.*, "ALIGN-CCUS D1.4.3 Guidelines and Cost-drivers of capture plants operating with advanced solvents," 2020.

[11] A. J. Sexton, K. Fisher, C. Beitler, and G. T. Rochelle, "Evaluation of amine reclaimer operation and waste disposal from post-combustion CO_2 capture," in *Laurance Reid Gas Conditioning Conference*, 2016.