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

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Techno-economic evaluation and guidelines for solvent management

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Executive summary

This report discusses the development of a software tool to perform techno-economic calculations on different solvent management strategies, compared to baseline operation, in order to assess the feasibility of these different solvent management strategies. As a basis for this analysis, the results from the other work packages of the LAUNCH project on the evaluation of different solvent management strategies are used as much as possible, and assumptions are made where necessary. The solvent management strategies that are evaluated are: Bleed and feed, reclaiming (thermal and ion-exchange) and oxygen removal (DORA and N_2 sparging).

The software tool created by ALTRAD follows the following structure:

1. Obtaining baseline values on the kinetics of dissolved oxygen driven amine losses, based on experimental data and fixing stoichiometric factor based on long-term testing data;
2. Calculating oxidative degradation rates in absorber packing and sump and lean/rich heat exchanger for selected case;
3. Assuming thermal degradation and solvent de-activation rate;
4. Calculation of operational time before the solvent needs to be treated based on a threshold value;
5. Calculation of relevant parameters as input for sizing and costing;
6. Sizing and techno-economic analysis of different solvent management strategies.

An important assumption in the tool is that after a certain threshold is reached for solvent degradation (defined as a percentage of solvent lost through degradation), the solvent will need to be replaced (step 4). The tool is structured in such a way that during a campaign, no refills are performed and the solvent concentration decreases until the threshold is reached. This approach might not be fully realistic towards a real system, as more frequent solvent refills are expected to maintain desired capture rates. However, this approach does allow the comparison of simply replacing the solvent with the addition of several solvent management technologies. The model currently only considers the linear degradation regime of solvents, which are based on the long-term pilot testing results with MEA and CESAR1 at RWE Niederaussum [17] [18]. This means that the kinetic lab data on the oxygen reaction rate is linked to the long-term results obtained at RWE Niederaussum by means of a stoichiometric factor (linking the solvent reaction rate to the oxygen reaction rate), by the equation below, where α is the stoichiometric factor

$$r = -\frac{d[MEA]}{dt} = -\frac{1}{a}\frac{d[O_2]}{dt}$$

For MEA and CESAR1, a linear solvent degradation rate of 350 g/ton CO_2 and 200 g/ton CO_2 were selected respectively based on the results of long-term campaigns, giving a stoichiometric factor of 1.12 and 0.0055 respectively. Additionally, using the residence times in the absorber packing, absorber sump and lean/rich heat exchanger, the split of degradation between these sections are determined to be 94/6/0 % for MEA and 70/28/2 % for CESAR1 respectively. Defining these splits has a large influence on the results. For instance, a high split towards the absorber packing has a negative effect of the performance of oxygen removal technologies. It has to be indicated that the definition of these splits still requires more research, as there are high uncertainties around the actual division of these splits. Particularly, the degradation model lacks data at temperatures above 60ºC, therefore the representation of the lean/rich heat exchanger needs to be re-evaluated in a future model release. This could change the split in a direction to favour oxygen removal technologies.

When a solvent management option is selected in the tool, it can have an influence on different parts of the structure indicated above. Preventive technologies (like oxygen removal) have a direct effect on the oxidative degradation rate in step 2, while corrective technologies (e.g. thermal reclaiming) only have an effect on step 5 and 6 of the tool. This means that the preventive technologies have an effect on the lifetime of the solvent (time before the degradation threshold is reached), while the corrective technologies have no effect on the replacement times. This is a simplification, as LAUNCH campaigns have shown that corrective technologies

such as reclaiming will also influence the degradation rate. However, at this moment there is no model available to quantify this influence. The bleed and feed results of this study have to be interpreted with care, as this method is implemented in the tool as a continuous bleed and feed rate, to keep the solvent quality always on par. A big assumption here is that by following this approach, the linear degradation regime can be maintained, which is shown to be impossible in practice [19]. Using this linear approach, the bleed and feed management technology will give identical results to the baseline case study of replacing the solvent when the threshold is reached. This is a limitation of the tool, and should be updated in a next version so that bleed and feed can be more precisely evaluated.

For the techno-economic analysis performed in this study, the tool is used to work out several cases with the MEA and CESAR1 solvents, including cases with different flue gas compositions (CO_2 and O_2 concentrations), absorber (packing) designs and temperature profiles in the absorber, which all influence the extend of oxidative degradation in the process. A pulverized coal power plant, a Waste-to-Energy plant and a natural gas fired power plant were selected as the case studies. The results from the techno-economic analysis for these cases are discussed for MEA and CESAR1 separately.

MEA
The baseline case study for replacing the solvent every 235 days sets the basis to compare other technologies against. In the baseline case, the main cost driver is the cost for solvent replacement.

For thermal reclaiming, the study indicates that this technology cannot be cost competitive with the baseline case for any use case. The main cost driver of thermal reclaiming comes from the CAPEX of the thermal reclaimer. This could be mitigated, if thermal reclaimers could be offered on a rental agreement basis, as companies only need these units to be on site at times when reclaiming is performed (typically a few weeks per year). It has to be noted that no thermal reclaiming tests were performed within LAUNCH, and there are knowledge gaps that prevent a very comprehensive analysis of this technology. As an example, the avoided downtime for solvent replacement/troubleshooting by using a thermal reclaimer is not taken into account, as it could not be properly quantified. This, however, is known to be a major economic benefit of reclaiming. Next to economic factors, also ecological factors play a role. To this extend, thermal reclaiming could greatly reduce disposal of solvent. A more detailed analysis of thermal reclaiming is required to draw further conclusions on the effectiveness of thermal reclaiming for MEA systems (and solvent systems in general). A similar conclusion can be drawn for ion-exchange reclaiming. However, since the CAPEX investment for this technology is expected to be lower (while having similar efficiency), it gives better results than thermal reclaiming. Also here, more detailed analysis of the technology is required.

The oxygen removal technologies show relatively bad results for the MEA processes, as the vast majority of the oxidative degradation (94%) is calculated to be occurring in the absorber packing, where the oxygen removal technologies have no effect on. The OPEX numbers for DORA are consistently higher than the baseline case, indicating that in this specific case, the technology does not lead to a positive business case. For nitrogen sparging, the high nitrogen consumption leads to a worse business case, indicating that this specific technology needs to reduce its nitrogen usage before it can be considered against other technologies on a commercial scale. As stated above, more research is needed towards the division of degradation between the absorber packing, sump and lean/rich HEX before further conclusions can be drawn on the effectiveness of oxygen removal technologies for MEA systems. Once a new, extended version of the degradation model is available, it can be implemented in the tool for re-evaluation of these technologies.

CESAR1
The baseline case study for replacing the solvent every 700 days sets the basis to compare other technologies against. It has to be noted that this value is still quite conservative, as in the LAUNCH project, the RWE campaign with CESAR1 has shown that longer than 3 years of operation can be reached without a full solvent exchange [11].

For thermal reclaiming, the study indicates that this technology can be competitive to the baseline, as the OPEX for reclaiming is much lower than exchanging the solvent. This is mainly due to the high costs of the solvent (as compared to MEA), which are mitigated by reclaiming the solvent. While the CAPEX of the reclaimer still causes a high initial investment, breakeven point between 5 to 8 years can be expected. Similar

to MEA, this is still excluding potential other cost savings of reclaiming, like reduced downtime of the plant and shared/rental equipment. The ion-exchange gives even better results (breakeven point below 1 year), due to the lower initial investment and similar efficiency compared to thermal reclaiming. To determine a more accurate potential of thermal reclaiming and ion-exchange reclaiming for CESAR1, a more detailed case study is necessary to draw further conclusions on feasibility.

Regarding oxygen removal, the calculated degradation split between the absorber packing, absorber sump and lean/rich heat exchanger (70/28/2%) determine the efficiency of oxygen removal technologies. With 98% of the oxidative degradation occurring before the lean/rich heat exchanger, the downstream (of the absorber sump) oxygen removal technologies do not generate a positive business case, as the amount of degradation that can be prevented is limited. For the upstream (of the absorber sump) configuration, the DORA oxygen removal technology shows slightly lower OPEX than the baseline, with total costs similar to the baseline case to due to initial CAPEX investment required for this technology. Again, for nitrogen sparging, the nitrogen demand generates high costs for this case, hindering a positive business case. As mentioned before, if the division of the degradation between the different part of the process if different than calculated in this report, this could have a direct effect on the estimated effectiveness of oxygen removal technologies. A lower fraction of degradation in the absorber packing and sump would have a direct positive effect in the evaluation of the oxygen removal technologies installed upstream and downstream of the absorber sump. Further analysis is required to assess the full potential of the oxygen removal technologies for CESAR1.

Conclusions

ALTRAD has successfully developed a software tool to perform techno-economic calculations on different solvent management strategies, which allows to incorporate solvent degradation models to the design and assessment of solvent management technologies. The tool results reflect the different model assumptions. While the extensive campaigns of MEA (ALIGN) and CESAR1 (ALIGN and LAUNCH), including tests with different solvent management technologies, have greatly informed the current models, knowledge gaps remain that influence the conclusions.

This study is a clear first attempt in quantifying the effect of different solvent management strategies for different types of industries that are implementing carbon capture technology. While a fully functioning software tool is created, the results are very dependent on the input data, for which a lot of uncertainties are currently still present. Additionally, the tool has shortcomings regarding the calculation method and the implementation of the different solvent management technologies, which can be improved in a next version. Nevertheless, the tools generate initial insights in the effectiveness of several solvent management strategies, on which the carbon capture community can built their future endeavours towards researching and evaluating solvent management strategies. It also gives clear indications regarding future steps in the current models and technology developments, including the need to lower the nitrogen consumption for nitrogen sparging, evaluation of CAPEX saving strategies for thermal reclaiming (e.g., use of mobile rental units), and the relevance of degradation models for the evaluation of oxygen removal technologies.

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1 Introduction

1.1 Project overview

Lowering Absorption Process Uncertainty, Risks and Costs (LAUNCH) is a three-year international collaborative research project aimed at accelerating the implementation of carbon dioxide (CO_2) capture across industry and enabling the development of novel solvents to support widespread deployment of carbon capture, utilisation and storage (CCUS). This will contribute to the acceleration and maturation of CCUS technology with respect to solvent degradation management.

A number of previous projects, including Enhanced Separation and Recovery of CO_2 (CESAR, 2008-2011), have monitored solvent degradation, corrosion and emissions. Most recently the ERA-NET ACT Accelerating Low Carbon Industrial Growth through CCUS project (ALIGN, 2017-2021), led by TNO, has developed the case for the use of second-generation solvents such as CESAR1 and proposed options to extend solvent life.

Making use of a range of pilot test facilities the LAUNCH project will investigate a number of novel degradation management strategies for a variety of solvents and operating conditions; and compare the costs of applying these with established solvent management strategies e.g. bleed and feed.

1.2 Report objectives

Work Package 6, led by Altrad Babcock, comprises two main objectives:

- A techno-economic evaluation that categorises several solvent degradation management options, highlighting the optimum concepts against agreed benchmarks [ALTRAD, TNO, RWE, BEFORM]

- The cost of solvent development based on the LAUNCH solvent qualification program will be determined with the target marginal cost set at €100k per solvent [TNO].

WP6 utilised the prediction and control methods identified in WP1 and WP2 along with the solvent qualification program recommendations from WP3 (Closing Degradation Knowledge Gaps). Where possible feedback on performance informed through testing in WP4 (Development) and WP5 (Demonstration) was used to validate any assumptions made.

The purpose of this document is to define and report the techno-economic analysis and solvent management guidelines associated with deliverable D6.1.2 and milestone M6.1.2.

2 Baselines and CO_2 capture plant

2.1 Benchmarking of PCC plant costs

A benchmarking exercise was carried out to review post combustion capture (PCC) total plant cost (TPC) from various sources in the last 15 years; the majority of data being less than 5 years; and select baseline plant of representative type, scale and performance.

Published cost and performance data for pulverised coal (PC), combined cycle gas turbine (CCGT), energy from waste (EfW) and cement plant from studies by established sources such as IEA [1], NETL [2], ETI [3] and BEIS [4] [5] as well as collaborative; ALIGN [6] and US-DOE [7]; and commercial; Bechtel [8] and Doosan Babcock; estimates were benchmarked to Q4 2021 according to the IHS Downstream Capital Cost Index. A variety of first - monoethanolamine (MEA) - and second-generation solvents were used on single and double (2 x 50%) train plant, typically to a CO_2 capture level of 90%.

With the availability of detailed process model input being critical to this study the PC and EfW cases from ALIGN and the US-DOE Sherman study were identified as potential candidates.

The adjusted total plant costs in Euros at Q4 2021, typically to Association for the Advancement of Cost Engineering (AACE) Class 4; -30% to +40% [9]; are graphed against daily carbon capture rate in Figure 1.

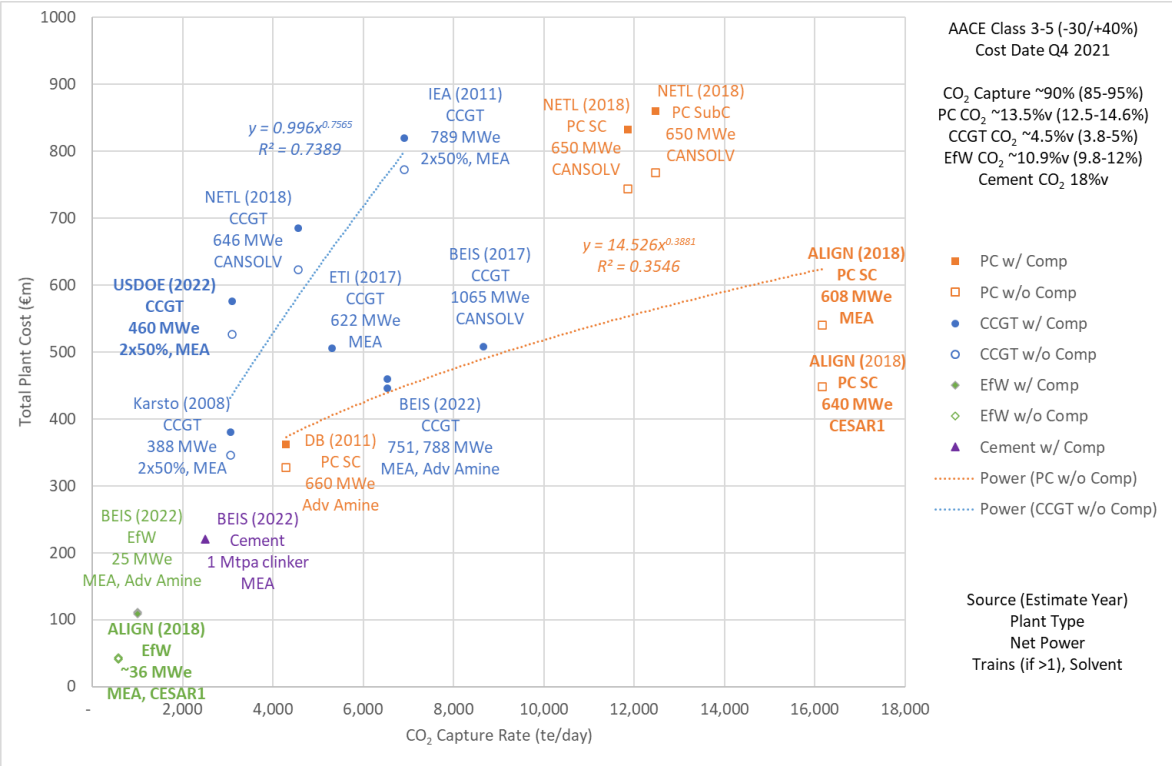


Figure 1 *PCC total plant cost (€m) versus daily CO_2 capture rate*

Considering the degree of scatter expected from these estimates, the correlations for PC and CCGT PCC plant costs with no compression are deemed to be reasonable. The cost of CO_2 compression to ~100 barg corresponds to a ~10% increase in total plant cost, although the BEIS CCGT with CO_2 compression figures are noted as outliers to the general cost trend.

The use of second-generation solvents is expected to reduce auxiliary plant size, and therefore cost, as a result of lower energy (reboiler steam) and electricity demand. This will be contributing to the noise around

the data presented here but potential reductions of 3 and 17% are evidenced by the BEIS (2022) and ALIGN respectively.

PCC plant costs for EfW and cement at low capture rates track backwards from the PC trend line. Plotting the same data for PC and CCGT only as specific plant cost per unit electrical output (Figure 2) shows that the increased net efficiency of CCGT plant (~52% versus ~32% LHV for PC) compensates for the increased capital cost of the PCC plant due to lower flue gas CO_2 concentration (~4.5% versus ~13.5% vol). For CCGT, the most recent BEIS data (2022) equates to ~€600/kW_e versus ~€1000/kW_e for comparable scales from other references.

The ALIGN PC plant cases are at the upper end of capture rate (~6 Mt/yr). Whilst these costs could be considered low, on the other hand the NETL figures could be deemed to be high within the margin of error (-30/+40%). The Sherman CCGT plant data are at the upper end of the CCGT specific plant costs, due in part to the twin absorber arrangement.

The ALIGN PC and EfW and Sherman CCGT plants were judged to represent a typical range of scale, flue gas composition, capture rate and solvent option suitable for evaluating the additional costs of solvent degradation management.

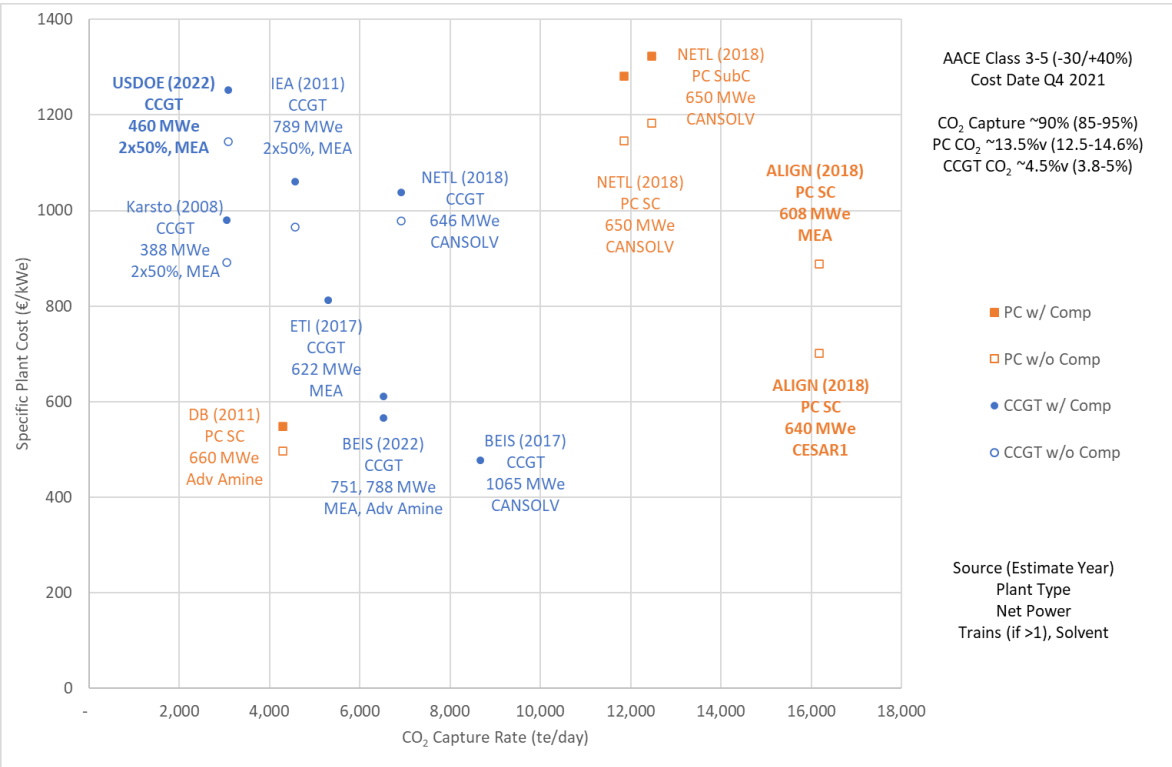


Figure 2 *Specific total plant cost (€/kWe) versus daily CO_2 capture rate*

2.2 Baseline plant

Table 1 summarises the selected base cases for coal, energy from waste and gas turbine plant.

Table 1 *Baseline plant summary*

Base case	1	2	3	4	5	6
Plant	PC			EfW		CCGT
Rating	1000 MW_e			200 kt/yr		420 MW_e
Reference	ACT ALIGN			ACT ALIGN		Sherman
Estimate	Class 4/5			Class 4/5		Class 3
Cost year	2018			2018		2021
O_2, CO_2 (%vol)	3.5, 14.6			7.9, 9.8		12.1, 3.9
Solvent	MEA	CESAR1	CESAR1	MEA	CESAR1	MEA
Concentration (%wt)	29.5	39.3	39.3	29.5	39.3	35
Capture (%)	90	90	95	90	90	85
Capture ($ktCO_2$/yr)	5,900	5,900	6,200	215	212	1132
Availability (%)	85	85	85	90	90	57
Total plant cost (M€)	489	405	382	19.9	20.5	477
Capture cost (€/tCO_2)[1]	32.2	31.5	31	35.7	37.6	115.7[2]

[1] With original solvent management OPEX (MEA 200 days, CESAR1 400 days solvent life)
[2] With original solvent management CAPEX and OPEX (reclaimer)

In all cases the PCC plant includes a direct contract cooler, water wash section and no compression of the CO_2 product, with the exception of the latter for the CCGT case.

2.2.1 Pulverised coal

The PC reference plant is a 1000 MW_e lignite-fired supercritical power plant unit (278 bar, 600°C), as modelled and reported within the ALIGN project [6] and typical of new thermal plant in central Europe. The plant features a wet flue gas desulphurisation (FGD) system unit for SO_x removal. Without coal pre-drying the baseline plant is capable of achieving a net efficiency of 43% LHV.

The post-combustion capture plant was designed to achieve 90% carbon capture (5.9 Mt/yr under continuous operation) with MEA and CESAR1 solvents, with further simulations carried out for CESAR 1 at 95% and 98% capture. At 90% capture net plant efficiency reduced to 32.5% and 34.3% LHV for MEA and CESAR1 solvents respectively. This corresponded to a respective cost of CO_2 captured of 32.2 and 31.5 €/tCO_2 and specific energy consumption for CO_2 captured of 3.37 and 2.66 GJ/tCO_2. For CESAR1 at 95% capture there was found to be no additional penalty to specific energy consumption.

As part of the techno-economic analysis sensitivities were carried out to CESAR1 solvent life (from 400 days to 4 years with activated carbon and particle filters) and other emissions management techniques, with a dry bed recommended at that time.

2.2.2 Energy from waste

Typical of the European average a hypothetical waste incinerator plant having a capacity of 200 kton of municipal solid waste per year was defined and modelled in [6]. A furnace, waste heat recovery and combined heat and power (CHP) system were integrated. Maximum steam conditions were 40 bar and 400°C. The plant would be able to generate 10.25 MW of electricity and 47.22 MW of district heating. Gross efficiency without carbon capture is 80.9%.

The post-combustion capture plant was designed to achieve 90% carbon capture (212 kt/yr) with MEA and CESAR1 solvents. With MEA, gross plant efficiency was reduced to 48%, whilst CESAR1 achieved a figure of 54.1%. Carbon capture cost for MEA and CESAR1 was 35.6 and 37.6 €/tCO_2 respectively, the higher cost of the advanced solvent offsetting the reduced reboiler duty in this smaller plant.

2.2.3 Combined cycle gas turbine

To complement the PC and EfW cases a CCGT reference plant was sourced from open literature [7]. The Sherman power plant is a 758 MW_e gas plant with F-class gas turbines in the United States.

The post-combustion capture plant was sized to capture 85% of the CO_2 (1.1 Mt/yr) from a flue gas equivalent to 420 MW_e using 35% wt MEA. The PCC plant features two absorbers, CO_2 compression and a two-stage semi-continuous thermal reclaimer. It should be recognised that the high stripper temperature (130°C) being employed in conjunction with this solvent could have implications for degradation.

Carbon capture cost is equivalent to 115.7 €/tCO_2 due primarily to a very high cost of capital (84 €/tCO_2) that is exacerbated by the capacity factor of 57% (5,000 hours per annum). Specific energy consumption of the PCC plant is 3.65 GJ/tCO_2.

3 Solvent management

3.1 Solvent degradation

Solvent degradation in post-combustion CO_2 capture is generally categorized into oxidative and thermal degradation. Thermal degradation occurs mainly at high temperatures (~120-130°C) in the stripper, whereas oxidative degradation occurs in the absorber at lower temperatures (~40-75°C). The oxidative route is complex in nature, with the solvent first reacting with oxygen to form primary degradation products, such as organic acids known as heat stable salts (HSS), and ammonia, from which some can further react to form secondary degradation products. Heat stable salts are non-regenerable and might accelerate corrosion. Metals such as iron and nickel leaching into the solvent system can initiate an auto-oxidative degradation mechanism. These degradation pathways combine to reduce the solvent's CO_2 capturing capacity.

3.2 Oxidative degradation model

During the LAUNCH project, TNO tested the direct oxidation of clean MEA and CESAR1 solvents in their ODIN apparatus in order to derive a degradation network model (DNM). During these campaigns, for a given CO_2 loading, the reduction in dissolved oxygen across at least three temperatures was measured. Least square correlations of temperature dependent data were made to determine reaction order and kinetic parameters i.e. pre-exponential and activation energy for the studied ranges of CO_2 loadings. Oxidative degradation rate is equated to solvent degradation via a stoichiometric factor, *a*, for the purpose of calculating a baseline oxidative degradation rate e.g. for MEA:

$$r = -\frac{d[MEA]}{dt} = -\frac{1}{a}\frac{d[O_2]}{dt}$$

More information on the background and limitations of the DNM can be found in [10].

The methodology applied for total degradation and the calibration of the model to existing pilot plant data are discussed in sections 5 and 6.

3.3 Solvent management technologies

The solvent degradation controls considered here and their current Technology Readiness Levels (on a scale of 1: Concept to 9: Normal commercial service) are shown in Table 2.

The benchmark options represent those techniques most commonly considered for solvent degradation management, whereas the more novel advanced techniques target specific species pertinent to solvent wastage by oxidative means via reductions in dissolved oxygen, NO_x or metals.

Table 2 *Solvent management techniques*

Type	Technique	Mechanism	Test Finding	Source	TRL
Benchmark (Corrective)	Bleed and Feed	-	-	-	9
	Thermal Reclaim	-	-	[8]	9
	Ion Exchange	-	Ionic and cationic	[11]	8
Advanced (Preventative)	Residence Time	Oxidative	Ambiguous	[12]	8
	DORA	Oxidative	90% O_2 reduction	[13]	5
	N_2 Sparging	Oxidative	90% O_2 reduction	[14]	5
	Thiosulphate	Oxidative	Ambiguous	[15]	5
	Non-metallic MOC	Oxidative	Insufficient data	[16]	4

Figure 3 presents a high-level process flow diagram (PFD) of the solvent management options initially considered for the study and their integration within a standard PCC plant. Note that non-metallic materials of construction are applicable to all process lines and equipment for this option.

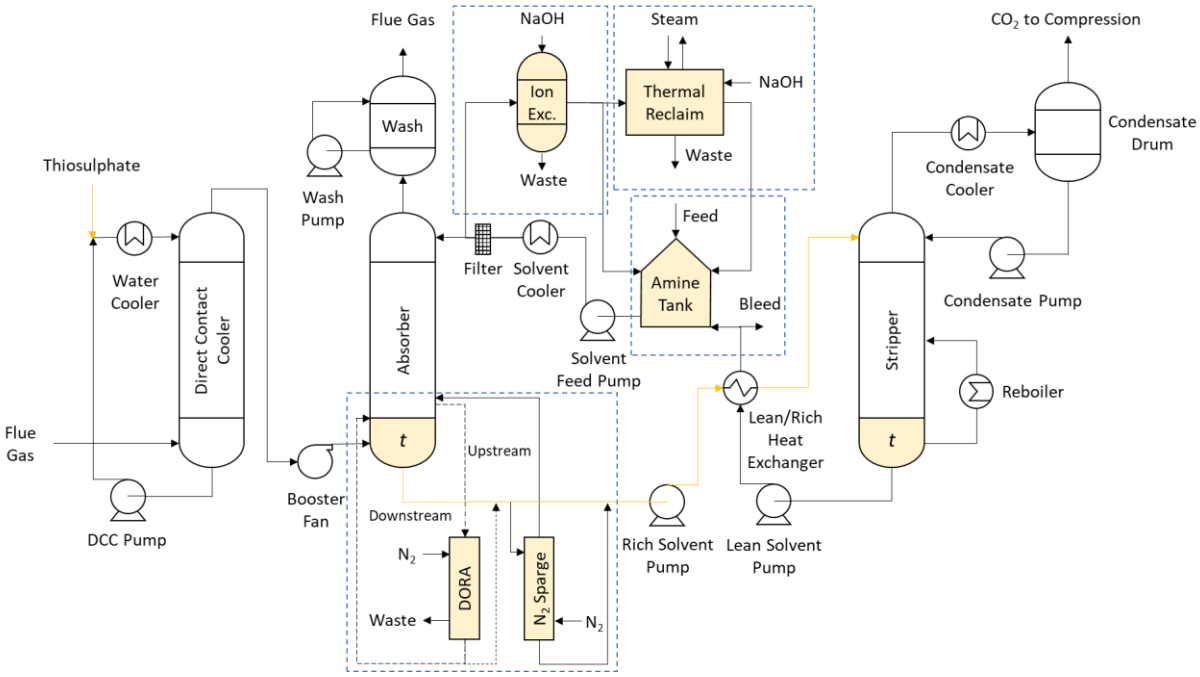


Figure 3 High-level process flow diagram of all solvent management options considered

The following sections describe these measures, equipment requirements and their shortcomings. Each mitigation measure can be applied separately or in combination with others.

3.3.1 Bleed and feed

Bleed and feed is a conventional practice where a portion of the degraded solvent is purged from the process and replaced with fresh solvent to maintain a manageable level of degradation.

3.3.2 Thermal reclamation

Thermal reclamation is a common practice to mitigate solvent degradation and involves distillation of either the full solvent inventory or a slipstream of the lean amine using steam before it is returned to the absorber column. Refer to the process flow diagram in Figure 4.

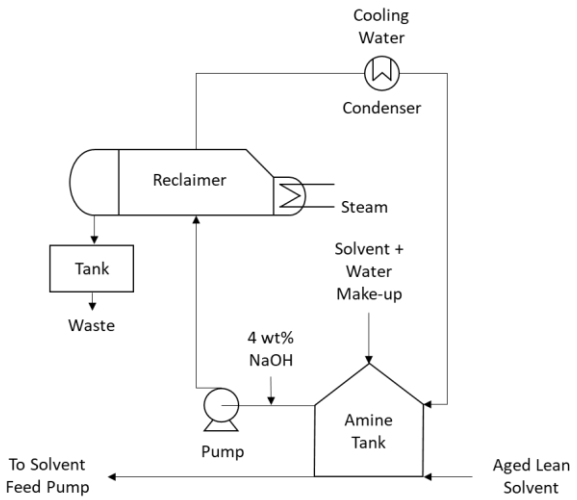


Figure 4 Basic process flow diagram for thermal reclaimer

Heavier products (including heat stable salts formed from the application of a caustic solution of sodium hydroxide) are separated from the amine and can be pumped and cooled ready for disposal. The condensed amine and water are returned to the lean amine tank. In this study, a simplified model for a thermal reclaimer is used, and an amine and water recovery of 95% is assumed, with all impurities remaining in the waste phase of the thermal reclaimer.

3.3.3 Ion exchange

Ion exchange utilises anionic and/or cationic resins to remove dissolved metal ions i.e. Fe, Ni, Zn, Cu, as well as anionic compounds e.g. Cl, NO_3, SO_4, and liberates amine from oxidative degradation products in the form of heat stables salts using a caustic solution (sodium hydroxide). Refer to the PFD in Figure 5.

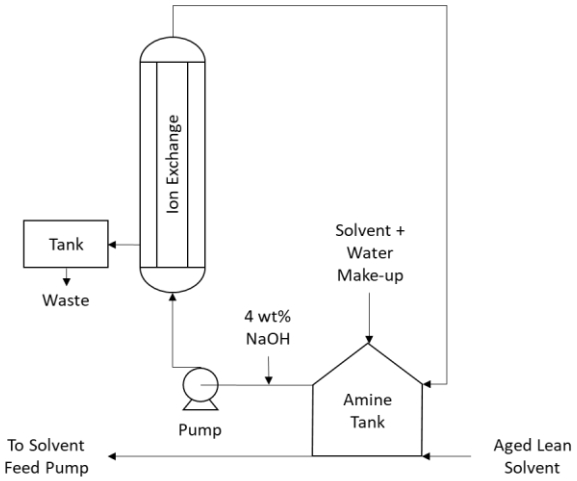


Figure 5 Basic process flow diagram for ion exchange

From RWE's experience on their 7.2 tCO_2/day pilot plant at Niederaussem a removal efficiency of ~90% of all ions is achievable [11]. There exists concern that the rate of degradation could accelerate following removal of 'protective' by-products with ion exchange (either anionic or cationic and anionic). A net removal of degradation products per cycle equal to 0.03%wt of the total inventory is defined.

3.3.4 Optimised residence time

Control of residence times in the absorber and sump, as well as interconnecting pipework, particularly on hot rich solvent line, is expected to have an impact on reducing oxidative degradation rate. Reduced plug flow residence times can be achieved via column sump redesign, shorter and/or small-bore pipework, or changes to process operating conditions.

Limited data from pilot and demonstration plant testing meant that this method was excluded from the TEA. However, it is noted that the variation of residence time is implicit within the calculation of oxidative degradation. A head-to-head comparison of LAUNCH rig #2 (1 kg/h) and RWE's pilot plant (7.2 t/day carbon capture) was conducted under WP5 with CESAR1 solvent [12]. The differences in residence times in key parts of the plant are identified in Table 3. Despite these differences, and some discrepancies in copper and nickel concentrations, similar absolute levels of organic acids and inorganic anions were found with the comparable temperature profile targeted through the absorber and sump.

Table 3 *Comparison of residence time (minutes) between RWE pilot plant and LAUNCH rig #2*

Plant	RWE Pilot	LAUNCH rig #2
Absorber sump	8	33
Cross heat exchanger	0.35	-
Cross heat exchanger to stripper	2	1.4
Total plant inventory	60	88

3.3.5 Dissolved oxygen removal apparatus

Dissolved oxygen removal apparatus (DORA) is a non-invasive process which makes use of a membrane contactor to remove oxygen from the rich amine leaving the absorber column, either upstream or downstream of the sump. Figure 6 presents the PFD for DORA. The main equipment required are the column(s), modular membranes (50 m^3/hr per unit for 3M LiquiCel EXF series), resized rich solvent pump(s), vacuum pump(s) and nitrogen supply tank and vaporiser. A sweep gas (nitrogen) flow rate of 4 m^3/hr is required per module.

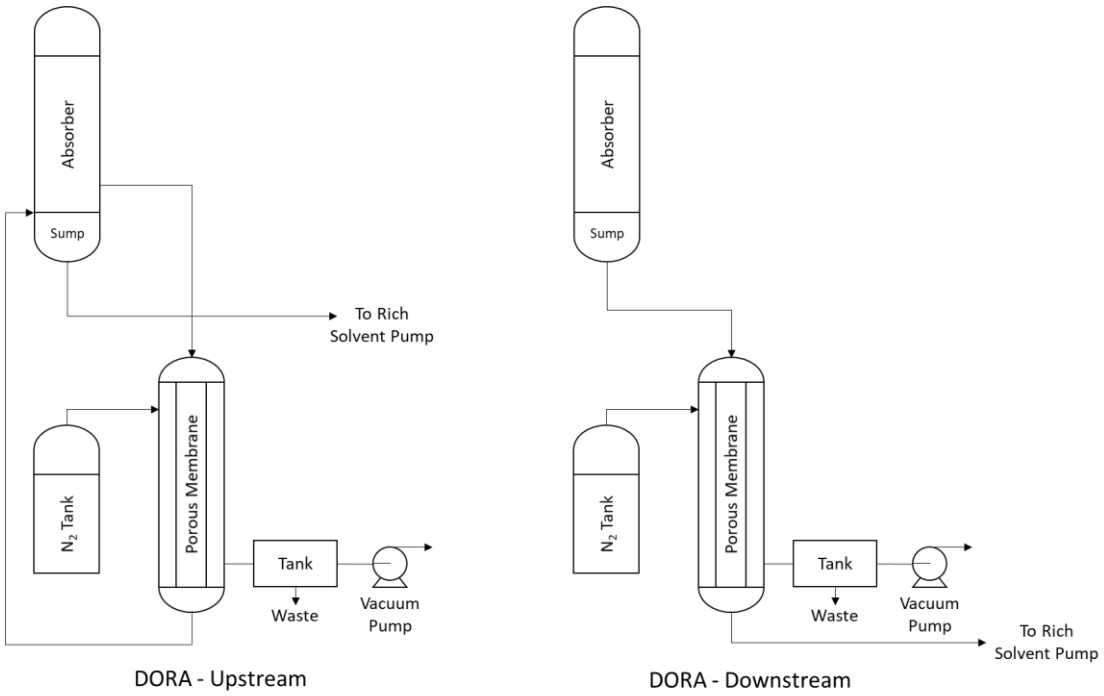


Figure 6 Basic process flow diagram for DORA (upstream and downstream)

From LAUNCH rig testing [13] DORA has been shown to reduce dissolved oxygen concentration in the solvent by ~90%. Although solvent-independent in theory thus far it has only been proven for MEA.

3.3.6 Nitrogen sparging

As another technology aimed at reducing dissolved oxygen content, nitrogen sparging features the introduction of bubble removal cap and nitrogen sparging grid in the absorber sump. Key equipment required includes the vessel(s), rich solvent pump(s) and a nitrogen supply tank and vaporiser. Figure 7 presents the PFD for nitrogen sparging. Total nitrogen flow rate is expected to amount to ~0.1% of flue gas volumetric flow, though it may be possible to further reduce this.

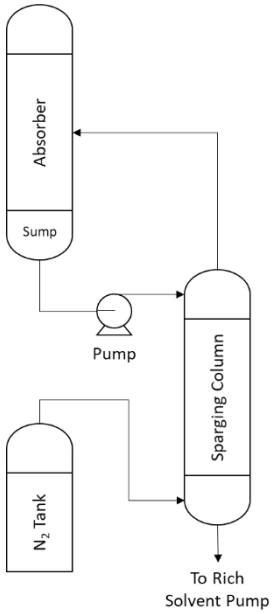


Figure 7 Basic process flow diagram for nitrogen sparging

From testing undertaken by the University of Texas on piperazine solvent [14], N_2 sparging was shown to be capable of reducing dissolved oxygen content in the solvent by 90%.

3.3.7 Thiosulphate dosing

As a technique to reduce NO_2 concentration, thiosulphate (S_2O_3) can be introduced with NaOH in the existing SO_2 polishing scrubber or DCC.

A significant reduction in NO_2 species concentration (up to 90%) can be affected through thiosulphate dosing [15]. However, concerns exist regarding the effect on degradation and nitrosamines. Therefore, this method was excluded from the TEA.

3.3.8 Non-metallic materials

The application of plastics as a material of construction for as much of the PCC plant as possible would significantly reduce any metal contaminants issue.

Operational issues, including high leakage rates, during testing of the plastic rig meant that limited data could be gathered [16]. As a result no firm conclusions on the impact of non-metallic plant construction could be drawn and this method was therefore excluded from the current study. However, the potential savings from using non-metallic materials holds promise [16].

3.3.9 Other

Activated carbon can be used to remove metals such as Fe and Ni from the lean amine returning to the absorber. Whilst Fe and Ni concentration can be reduced there may not be a discernible effect on degradation rate e.g. as found for CESAR1 [11]. Iron will ultimately be limited by the amount dissolving into the system or inadvertently supplied with the fresh amine.

It is assumed that particle filters only are included to control the emissions from both solvents.

Figure 8 presents a high-level process flow diagram of the solvent management options taken forward to TEA.

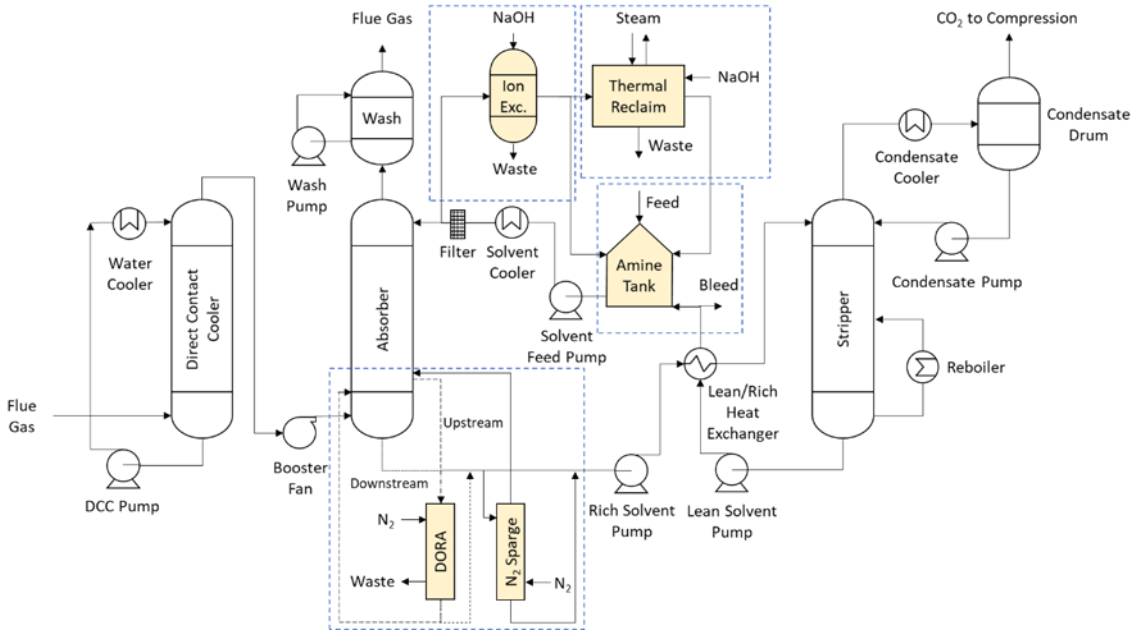


Figure 8 High-level process flow diagram of all solvent management options taken forward to TEA

4 Cost estimation methodology

4.1 Economic basis

The reference plant are assumed to be in Western Europe.

4.1.1 Currency

The reference currency is the Euro, €. Costs in other currencies are converted using the average annual exchange rate for that year.

4.1.2 Base year and escalation

The base year for cost reference is 2021 (Q4). Where costs have been sourced from periods other than this these have been escalated using the EU Harmonised Index of Consumer Prices, HICP.

It is assumed that any new plant is a nth of kind commercial offering and has already been constructed in the preceding four years e.g. in this study total plant cost is relevant for 2022.

4.2 Capital cost estimate

The capital costing of the solvent management technology equipment required for integration with the host plants was prepared as an AACE Class 5 estimate with an accuracy of -50% to +100%, assuming 0% to 2% full project definition [9], equivalent to a conceptual design.

With the exception of the DORA membrane modules, the main equipment identified for each preventative technology in section 3.2 was sized and costed relative to reference plant and using a typical power exponent of 0.65:

$$Scaled\ cost = Reference\ cost \left(\frac{Qscale}{Qreference}\right)^{0.65}$$

where Q is solvent volumetric flow rate.

For each case the number of columns and rich solvent pumps was retained per the original PCC plant design. A single nitrogen supply tank and vaporiser was assumed for each scenario based on a 400 m^3/hr reference on a three-year rental. A 50% saving on the standalone vessel cost of DORA downstream was assumed for the upstream option based on the technique being integrated at design.

Semi-continuous operation of a slipstream was assumed for the sizing of the corrective measures; thermal reclaim (0.13% wt) and ion exchange (4% wt), with capital cost of a total EPC package scaled per above rule on this basis. No additional capital costs were associated with bleed and feed.

Total plant cost for solvent management techniques was arrived at using Altrad Babcock normal factors for installation, construction, engineer procure construct (EPC) and includes a contingency of 40% in line with the estimate class. By this means TPC corresponds to approximately 4x main equipment cost.

4.3 Operating and maintenance costs estimate

Fixed and variable operational expenditure (OPEX) parameters are shown in Table 4. For fixed OPEX it was assumed that operating and administrative labour was as per the existing PCC plant, therefore only additional insurance, tax and maintenance costs are accounted for.

Table 4 *Operational expenditure parameters*

Type	Parameter	Value	Reference
Fixed OPEX	Insurance and local taxes	2% TPC	ALIGN project
	Maintenance	2.5% TPC	ALIGN
Variable OPEX	Heat	4 €/GJ	ALIGN
	Electricity	0.1 €/kWh	ALIGN
	Process water	1 €/t	ALIGN
	MEA, CESAR1 solvent	2100, 8100 €/t	ALIGN
	NaOH	2100 €/t	ALIGN
	Solvent disposal	200 €/16t	ALIGN
	Reclaimer waste disposal	375 €/t	ALIGN
	Bulk nitrogen	0.2 €/t	Altrad Babcock
	DORA membrane replacement	8000 €/unit	TNO/3M
	Ion exchange resin replacement	1000 €/unit-yr	MIONTEC

A pump electrical efficiency of 76% was assumed. Solvent, water, sodium hydroxide, waste and utility requirements (cyclical in the case of corrective measures) are used with plant availability in the calculation of annual variable operating cost.

For ion exchange a specific energy requirement of 0.6 kWh/m^3 was used. Modular elements with limited lifetime such as DORA membrane and ion exchange resin were costed without any bulk discounts.

4.4 Cost of carbon capture

The net present value over the plant life is calculated using a discount rate of 8% and this is used to calculate a levelised cost of carbon capture (€/tCO_2) as follows:

$$CCC = \frac{TPC + \sum_{i=1}^{n} \frac{O\&Mi}{(1+r)^i}}{tCO_2\ captured}$$

where TPC is total plant cost, O&M is operating and maintenance costs in year i, and r is the discount rate.

4.5 Economic assessment

The overall methodology is to calculate capital and operational expenditure for the integration of solvent degradation control measures over and above the reference PCC plant costing determined previously in [6] and [7].

The reference total plant costs and annual operating and maintenance costs were updated to exclude any solvent management, consumables, replacement and waste, and where applicable, escalated to end 2021 and converted to Euros. The cost of capture is inclusive of financing of capital. Table 5 presents the adjusted figures.

Table 5 *PCC plant baseline costs excluding solvent management*

Base case	1	2	3	4	5	6
Plant	PC			EfW		CCGT
Solvent	MEA	CESAR1	CESAR1	MEA	CESAR1	MEA
Concentration (%wt)	29.5	39.3	39.3	29.5	39.3	35
Capture (%)	90	90	95	90	90	85
Capture (ktCO_2/yr)	5,900	5,900	6,200	215	212	1,132
Availability (%)	85	85	85	90	90	57
Total plant cost (M€)	489	405	382	19.9	20.5	463[1]
Fixed OPEX (M€/yr)	24	20	19	1.3	1.4	9.5
Variable OPEX (M€/yr)	1	3	4	3.3	2.6	8.4[1]
Total OPEX (M€/yr)	25	23	23	4.6	4.1	17.9
Capture cost (€/tCO_2)	30.3	25.6	25.1	36.6	34.8	85.9

[1] Including contingency on TPC but excluding CO_2 compression and thermal reclaimer.

5 Techno-economic tool

5.1 Methodology

Figure 9 summarises the calculation methodology in the tool as a block flow diagram. The tool consists of several parts:

1. Obtaining baseline values on the kinetics of dissolved oxygen driven amine losses, based on experimental data and fixing stoichiometric factor based on long-term testing data;
2. Calculating oxidative degradation rates in absorber packing and sump and lean/rich heat exchanger for selected case;
3. Assuming thermal degradation and solvent de-activation rate;
4. Calculation of operational time before the solvent needs to be treated based on a threshold value;
5. Calculation of relevant parameters as input for sizing and costing;
6. Sizing and techno-economic analysis of different solvent management strategies

When a solvent management option is selected, it can have an influence on different parts of the tool, as indicated per mitigation option in Figure 9. Below, the different parts of the tool are explained more in detail.

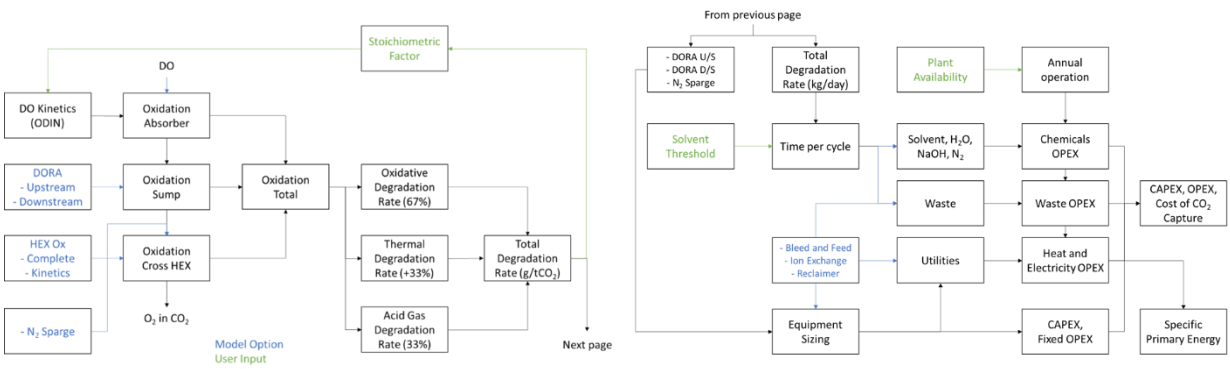


Figure 9 *Calculation block flow diagram*

5.1.1 Obtaining baseline values on the kinetics of dissolved oxygen driven amine losses, based on experimental data and fixing stoichiometric factor based on long-term testing data

For the baseline DO kinetics calculations, results from lab experiments of TNO are used, where the oxygen depletion rates are analysed for different solvents at several process conditions varying the oxygen concentrations, CO_2 loading and temperatures. Additionally, the stoichiometric factor for the selected solvent is determined, to relate the oxygen depletion rate with the solvent consumption rate. The stoichiometric factors for this study are fitted to the long-term results of the MEA and CESAR1 campaigns of RWE, and are shown in Table 6.

5.1.2 Calculating oxidative degradation rates in absorber packing and sump and lean/rich heat exchanger for selected case

The oxidative degradation rate for the selected case study is calculated in different parts of the absorber (absorber packing and sump) and the lean/rich heat exchanger.

For the absorber packing, the oxygen concentration is constant, as depleted oxygen is immediately replenished from the bulk gas phase. A temperature profile, CO_2 loading profile and solvent residence time profile throughout the column are used in the tool to calculate the reaction rate.

For the absorber sump, there is no constant replenishment of oxygen like in the absorber packing, which is taken into account in the model. The model calculations are similar, but the oxygen concentration decreases over time in the solvent. The residence time in the sump mainly determines the level of oxygen depletion that can be expected in the solvent, before the solvent is transferred to the lean/rich heat exchanger and the stripper.

Any oxygen remaining in the solvent after the absorber sump will be introduced into the heat exchanger. Unfortunately, currently there is no high temperature oxygen depletion experimental data (>60 °C). The tool offers two choices: (1) Use low temperature kinetics in the heat exchanger and (2) assume all remaining oxygen is reacted away in the lean/rich heat exchanger.

The three sections together determine the split of oxidative degradation that has taken place between the absorber and lean/rich heat exchanger. The tool assumes that no degradation occurs in the stripper, with the assumption that any remaining oxygen will be stripped from the solvent at these high temperatures.

The preventive oxygen removal technologies considered in this work (DORA and N_2 sparging) have an effect on the values calculated in this part of the tool.

5.1.3 Assuming thermal degradation and solvent de-activation rate

The current tool only includes a function for oxidative degradation, and there is no similar model for thermal degradation or solvent de-activation. In order to include thermal degradation and solvent de-activation in the case study (which are relevant for evaluating thermal reclaiming for instance), these are included as a percentage of the oxidative degradation. In the case studies for this report, the following distribution is used.

$$Total\ degradation rate = Oxidative\ (50\%) + Thermal\ (25\%) + HSS\ (25\%)$$

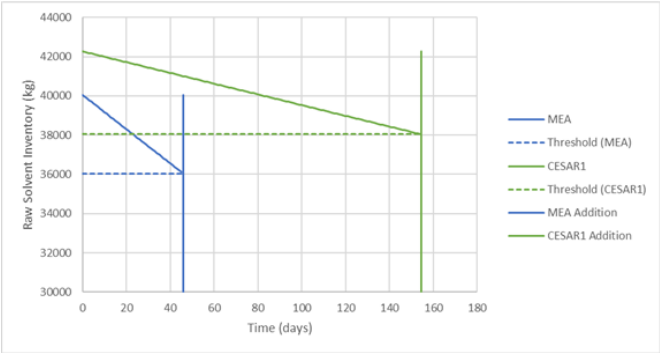
It has to be noted that this division of degradation types is arbitrary and can vary in reality. For instance, the thermal degradation is a strong function of the operation of the reboiler (operational stability, temperature level), and the amount of solvent de-activation by heat stable salts is a strong function of impurities in the flue gas.

5.1.4 Calculation of operational time before the solvent needs to be treated based on threshold value

Using the total degradation rate, the solvent quality over time can be evaluated. Please note that the tool only covers linear degradation, and no exponential degradation analysis is included. The active solvent in the inventory of the plant will decrease over time. The user can set a certain threshold before the solvent needs to be treated, shown in Figure 10. The model does not include (continuous) replenishment of the solvent while in operation, which is one of the major limitations of the current model developed in this project. This method can bring problems in the evaluation of the solvent management strategies in multiple ways. Examples are:

- When a solvent is very stable (like CESAR1), more solvent than the original inventory might have been reacted away before solvent treatment is necessary (in practise, the solvent concentration is kept stable by adding solvent regularly). This situation cannot be simulated with the current tool.

- When the solvent composition is important for the solvent management strategy (e.g. thermal reclaiming), a low active solvent concentration might cause wrong interpretation of the results of the management strategy, as in normal operation, the solvent concentration is different than what the tool suggests.



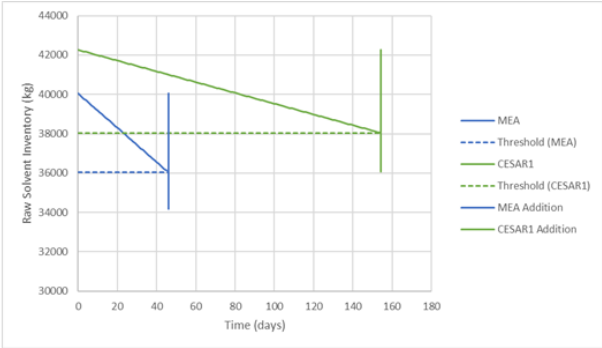


Figure 10 *Sample solvent degradation and replenishment profiles for baseline (lhs) and reclaiming*

Where complete oxidation has not been selected as an option under heat exchanger input the residual O_2 in CO_2 product is reported.

5.1.5 Calculation of relevant parameters as input for sizing and costing

Depending on the input parameters selected, and the solvent management strategy selected, relevant process parameters will be calculated that serve as input for the sizing and costing of the different solvent management strategies. Important parameters for the preventive and corrective solvent management technologies are calculated here.

5.1.6 Sizing and techno-economic analysis of different solvent management strategies

Based on the results of the model, the relevant additional equipment for that specific case is sized, and a techno-economic analysis is performed on the (additional) equipment in the capture plant, and an analysis of different solvent management strategies can be performed.

5.2 Software application

A software application was developed to facilitate the techno-economic evaluation. The software brought together the various experimental data sets, models, process model output and expertise from the individual project partners into a consistent and unified form. Other key requirements were version control, ease of access and secure storage. Hence, a web-based application was chosen as the preferred method.

The application was written in the Python programming language and consists of two main components: a calculation engine and a web application 'wrapper'. The calculation engine contains the technical logic and know-how obtained from the project whereas the web wrapper provides a simple interface to the calculation engine that a user can access via a standard web browser. In addition, the application also connects to a relational database (PostgreSQL) in order to store calculation inputs, outputs, etc.

Each calculation run requires a large number (>100) of user-defined inputs. Each input variable is mapped to a particular attribute in one of the database tables. The first part of the calculation process involves the formatting and validation of input values passed to the calculation engine from the web interface. In the next step, the appropriate calculations are performed based on the user selection. For example, the user has a choice to include or exclude DORA / N_2 Sparging, Bleed Feed and Reclaim / Ion Exchange options. The individual calculations and equations are not computationally expensive, with a complete calculation run taking less than a second to complete. In the final step, calculation inputs and outputs can be saved to the database if selected by the user.

The database was pre-populated with default input values for the baseline techno-economic scenarios and a limited number of other solvent management scenarios. This enables a user to simply select a database record instead of carrying out the laborious task of manually entering the inputs for a single calculation run. Nevertheless, it was not feasible to pre-populate the database with all of the input configurations required for the project's overall analysis. To alleviate this issue, the calculation engine can also be operated in 'bulk' mode

in which the desired scenario inputs are constructed through the selective combination of the pre-populated values. This allows all of the desired scenario calculations to be run at the same time. The bulk processing method can only be employed programmatically and is not available to users via the web interface.

The web application was created using the Django web framework. Django provides server-side functionality such as URL routing, authentication, security, database management etc. In addition, HTML / CSS and Javascript were used to develop the client-side user browser interface. The inputs are grouped under 10 different categories: 1. Costing Input; 2. Engineering Constants; 3. Calculation Setup; 4. Dissolved Oxygen; 5. ODIN Model; 6. Absorber Column; 7. Absorber-Sump; 8. Cross Hex; 9. Total Baseline Degradation; and 10. Solvent Management. A further category entitled ‘Output’ displays the output fields.

Project partners are able to select a database record from a hidden table via the ‘Select’ button at the top of the interface. The table lists the current saved calculations in the database and the list can also be sorted and filtered by a user. The selection of a record from the table will populate the input and output fields in the interface with the saved values. A user can perform a calculation using the ‘Calculate’ button and a new database record can be saved using the ‘Save’ button. Simple validation of the inputs is performed before a calculation is run and the user will be informed of any errors that need to be addressed before proceeding further. In addition, outputs can also be downloaded to a CSV file on the user’s local machine via the ‘Download’ button.

The web interface also provides two optimisation methods. The first is the optimisation of the ‘Clean Solvent Threshold’ via a user defined target value of the ‘Time to Reach Threshold’. The second is an optimisation of the ‘Stoichiometric Factor’ using a target value of the ‘Total Degrade Rate’. In each case, the ‘minimise_scalar’ function from the SciPy Python package was used to perform the optimisation.

6 Techno-economic cases and results

6.1 Calibration against RWE pilot plant

In order to better represent actual plant performance the degradation rate predicted by the oxidative degradation model for RWE's pilot plant at Niederaussem [11] [17] was calibrated to the (total) rates determined for MEA and CESAR1 solvents by adjustment of the stoichiometric factor. Table 6 summarises the results of this exercise using process model input for absorber, sump and cross heat exchanger. Flue gas oxygen was 4.6% vol and carbon capture ~90%.

Table 6 *Degradation model calibration against RWE pilot plant*

Pilot plant case	MEA	CESAR1
Total inventory (kg)	3283	3074
CO_2 capture (t/day)	7.2	7.2
DNM Baseline total degradation (g/tCO_2)	302	0.8
Stoichiometric Factor (-)	1.12	0.0055
DNM Calibrated total degradation (g/tCO_2)	350	200
Absorber/sump/HEX degradation rate split (%)	94 / 6 / 0	70 / 28 / 2
Solvent threshold (%)	40	15
Time (days)	235	700

As evident from the baseline calculation the total oxidative degradation rate is significantly higher for MEA. For both solvents the majority of oxidative degradation occurs through the absorber column where O_2 is higher. Although the kinetic rate for MEA peaks around a loading of 0.45, versus 0.2 for CESAR1, it is orders of magnitude greater for MEA. As such, the stoichiometric factor varies significantly between solvents. At the sump, degradation - absolute and relative - is higher for CESAR1. Notwithstanding the potential for oxidation through the rich solvent pipework, the low residence time of the rich/lean heat exchanger means oxidative degradation through this equipment is negligible for both solvents.

During both test campaigns solvent losses through sampling, degradation and emissions were replenished in order to maintain the ongoing operability of the capture plant. This is partially reflected in the low threshold levels of the original solvents. A differing threshold can be expected for CESAR1 by virtue of its increased solvent inventory (39.3 vs. 30%wt) and cyclic capacity. A MEA life of 235 days corresponds approximately to the end of the linear degradation period i.e. onset of exponential degradation as observed in the RWE pilot during the ALIGN project [17]. On the other hand, even an 800+ days life for CESAR1 did not result in uncontrolled degradation [11] and a relative lifetime for CESAR1 of ~3x that of MEA on the RWE pilot plant can therefore be considered conservative.

6.2 Cases

The matrix of cases run for each of the baseline plant cases (i.e. 16 x 6 = 96 cases in total) is tabulated below.

Table 7 *Case matrix per baseline plant case*

Type	Case	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
None	Baseline																
Preventative	DORA U/S																
	DORA D/S																
	N_2 sparging																
Corrective	Bleed and feed																
	Thermal reclaim																
	Ion exchange																

Although preventative and corrective measures can be applied in any combination the high efficiency of each individual technique means that it would be most cost-effective to consider those within the preventative and corrective categories to be exclusive. Thus, this study seeks to identify the most cost-effective corrective measure with or without a preventative measure.

6.3 Results and discussion

6.3.1 Baseline degradation characteristics

Based on the calibrated stoichiometric factors for each solvent Table 8 presents the oxidative degradation split, total degradation rate and time to the threshold levels given in Section 6.1 for the baseline cases. The maximum residual dissolved oxygen in the CO_2 product is also shown. Oxidative degradation rate and time to threshold is given in Figure 11.

Table 8 *Baseline cases 1 to 6 summary results*

Case	1	2	3	4	5	6
Plant	PC			EfW		CCGT
Solvent	MEA	CESAR1	CESAR1	MEA	CESAR1	MEA
Carbon capture (%)	90	90	95	90	90	95
Oxygen in flue gas (% vol)	3.5			7.9		12.1
Residence time (mins)						
Absorber	4	8.9	8.8	3.7	5.4	3.7
Absorber sump	6	6	6	6	6	8.9
Cross heat exchanger	0.11	0.09	0.09	0.19	0.25	0.15
Absorber degrade (%)	92.6	62.7	68.9	95.2	77.5	95.4
Absorber sump degrade (%)	7.3	36.8	30.7	4.7	21.6	4.5
Cross heat ex. degrade (%)	0.1	0.5	0.5	0.1	0.9	0.1
Total degrade rate (g/tCO_2)	184	136	161	627	431	1510
Time to threshold (days)	369	588	495	55	106	57
Max. O_2 in CO_2 (ppmv)	7	10	10	11	22	2

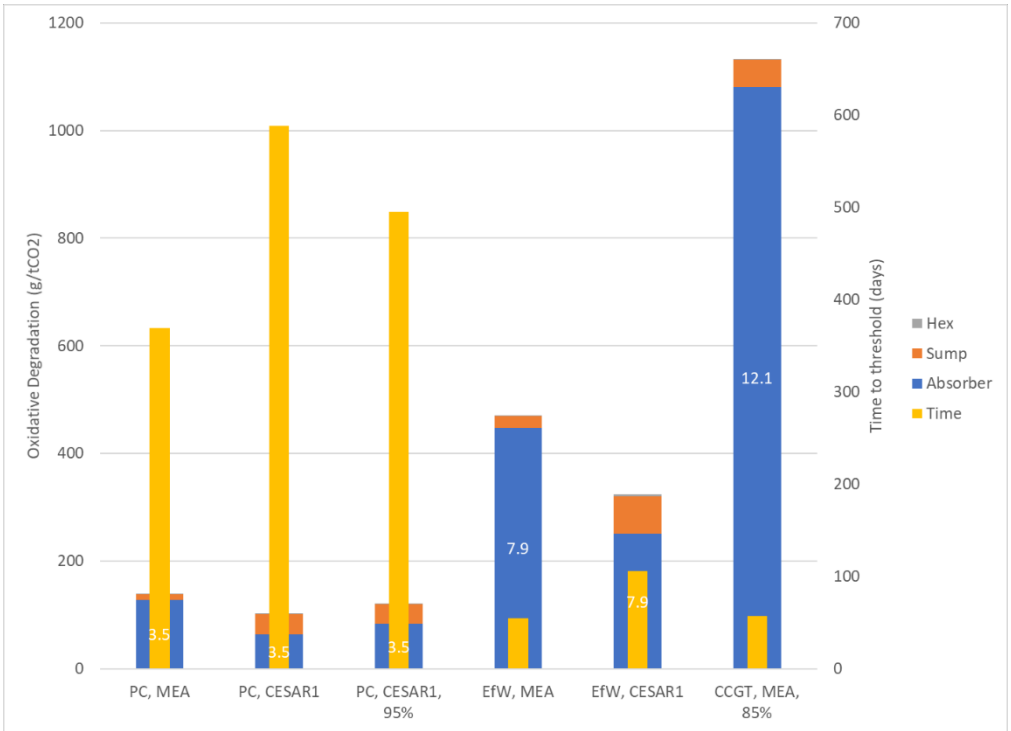


Figure 11 *Base cases 1 to 6 – total degradation rate and time to threshold*

Consistent with the pilot calculations oxidative degradation split is more prominent in the absorber for MEA and absorber sump for CESAR1 respectively. Based solely on the relative difference in flue gas oxygen alone, relative to the pilot results a 24% reduction degradation rate would be expected for the PC plant, whilst increases of 72% and 163% would be anticipated for the EfW and CCGT plant. Due to the specific design of each plant scenario (including differing loading, flow rate and inventory), and the effect of temperatures and residence times, the calculated degradation rate is 40-60% lower for PC, 34-62% higher for EfW, and 224% higher for CCGT. However, flue gas oxygen is the dominant factor, as apparent from the higher total degradation rates for the EfW and CCGT plant. This means a shorter time to reach the clean solvent threshold level for these plant. A solvent life for MEA of 55 days for the EfW plant is very low. Notwithstanding the uniqueness of the specific plants it is observed that the predicted degradation rate is in line with the range of 0.5-1 kg/tCO_2 from recent testing of a 100 kton/yr commercial carbon capture plant on a 30 MW_e waste to energy plant in Europe [19]. The use of CESAR1 solvent increases solvent lifetime by 60% and 93% for the PC and EfW plants respectively.

Oxygen in the CO_2 product is of the expected order of magnitude and acceptable for export (<100 ppmv). It is higher for CESAR1 cases due to the low temperature rate of consumption being lower.

6.3.2 Preventative technique effect

The total degradation rate and time to solvent replacement are shown for the preventative techniques in Table 9.

Table 9 *Summary of baseline and preventative solvent management technique effect on degradation*

Case	1	2	3	4	5	6
Plant	PC			EfW		CCGT
Solvent	MEA	CESAR1	CESAR1	MEA	CESAR1	MEA
Carbon capture (%)	90	90	95	90	90	85
Baseline degrade (g/tCO_2)	184	136	161	627	431	1510
Time to threshold (days)	369	588	495	55	106	57
DORA U/S degrade (g/tCO_2)	173	101	126	601	365	1451
Time to threshold (days)	393	790	629	57	126	59
DORA D/S[1] degrade (g/tCO_2)	184	135	160	627	429	1510
Time to threshold (days)	369	590	497	55	107	57

[1] Applies for N_2 sparging also U/S = Upstream, D/S = Downstream

For MEA solvent the very high proportion of oxidation occurring in the absorber column means little to no benefit from using a preventative technique. For CESAR1, however, the advantage of DORA being utilised upstream of the absorber sump is apparent from a 35% increase in solvent life for the PC plant, and 19% increase for the EfW plant (a lesser improvement for EfW being consistent with a higher oxygen level in the flue gas).

6.3.3 PC plant baseline costs

Incremental capital and operating costs on the three PC plant cases are given in Table 10. This considers no active solvent management other than a particulate filter.

Table 10 *PC plant base cases 1 to 3 summary results (net increase for solvent management)*

PC case	PCC plant	1	PCC plant	2	PCC plant	3
Solvent	MEA		CESAR1		CESAR1	
Carbon capture (%)	90		90		95	
Total plant cost (M€)	489	0.4	405	0.3	382	0.3
Fixed OPEX (M€/yr)	24	0.02	20	0.01	19	0.01
Variable OPEX (M€/yr)	1	3.30	3	6.62	4	8.23
Total OPEX (M€/yr)	25	3.32	23	6.63	23	8.25
Capture cost (€/tCO_2)	31.6	0.2 (1%)	26.9	0.4 (2%)	26.4	0.5 (2%)

Aside from the outlay and ongoing maintenance of the particulate filter, a minimum annual variable cost of 3.3 M€ is required for case 1. This is predominantly composed of the cost of fresh MEA solvent.

For case 2 the variable operating cost reflects the higher cost (8100 vs. 2100 €/t) of the CESAR1 solvent tempered by the reduced inventory and a 60% increase in the time to replacement. This increases the capture cost per tonne figure by 2% compared with 1% for MEA. At 95% capture, total annual operating costs increase by 24%, but the total cost of capture remains less than at the 90% capture level.

6.3.4 PC plant solvent management costs

Figure 12 presents the comparison of total capital (left hand axis) and operating costs (bubble size, €/yr) for the individual corrective and preventative solvent management options for PC cases 1 (MEA) and 2 (CESAR1).

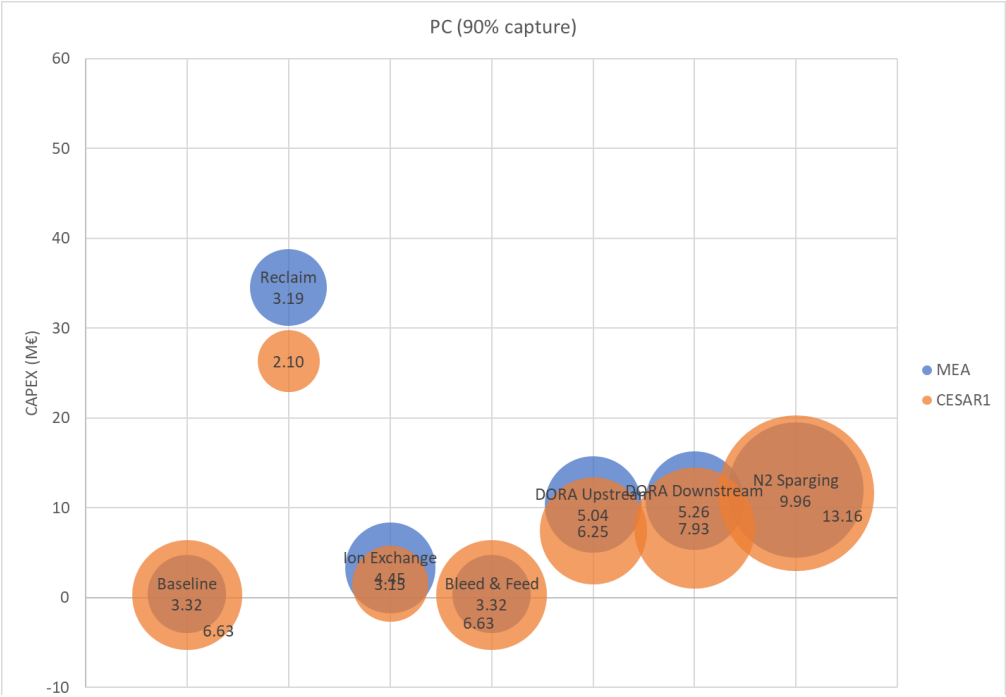


Figure 12 *PC plant base cases 1 and 2 – total plant cost and OPEX of solvent management options*

Of the benchmark techniques, due to its size and complexity thermal reclaiming presents a high plant cost for lower operating cost than the baseline, whilst ion exchange has low capital and operating expenditure. The operating costs of bleed and feed are identical to the baselines due to the optimal continuous rate being equivalent to the effective batch bleed and feed of replacing the solvent at end of life. Partly due to their novel nature the preventative techniques have notable capital and operating costs associated with them. Compared with MEA, all techniques incur lower capital costs for CESAR1. Operating costs of thermal and ion exchange follow suit, whereas operating costs for preventative techniques are higher for CESAR1.

Figures 13 to 15 present the breakdown of annual operating costs for the individual corrective and preventative solvent management options for PC cases 1, 2 (MEA, CESAR1; 90% capture) and 3 (CESAR1; 95% capture).

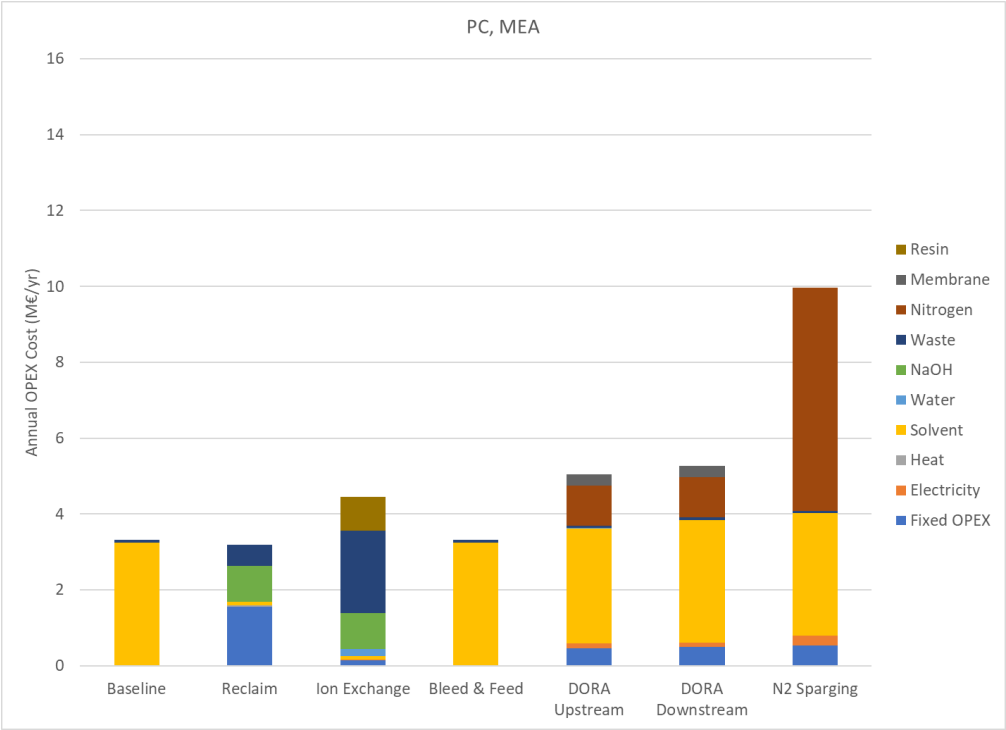


Figure 13 *PC plant base case 1 – annual OPEX breakdown of solvent management options*

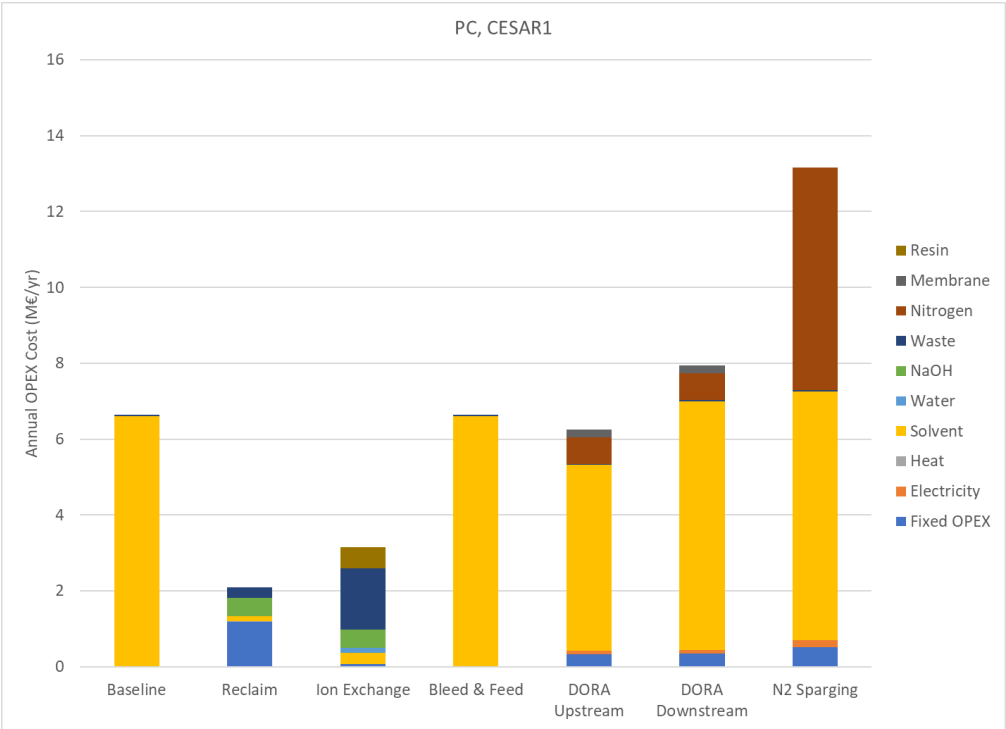


Figure 14 *PC plant base case 2 – annual OPEX breakdown of solvent management options*

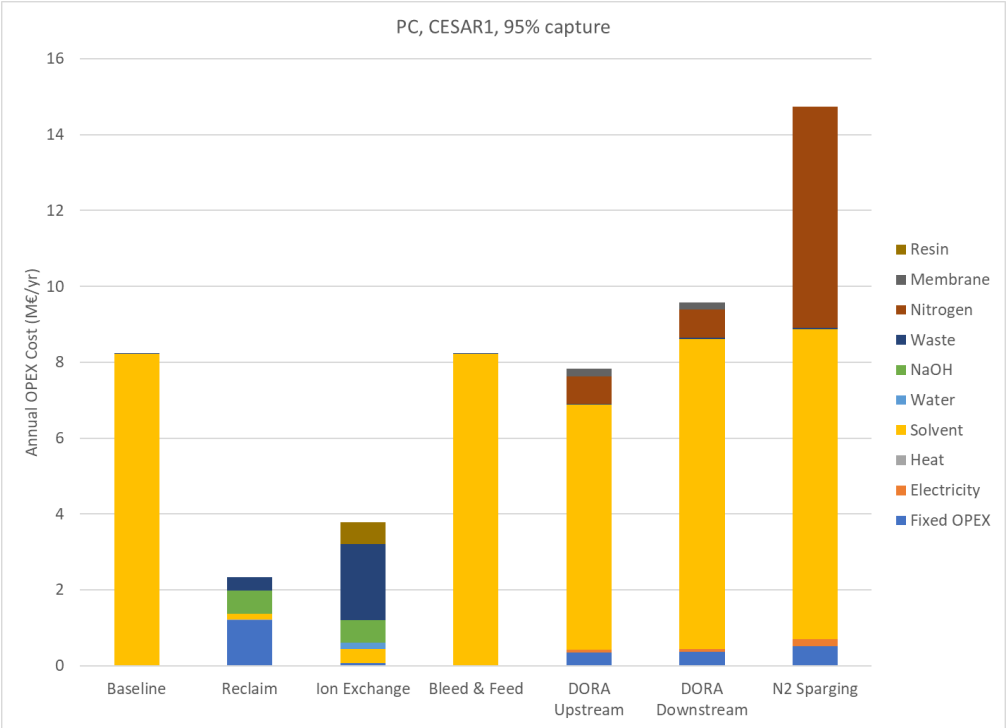


Figure 15 *PC plant base case 3 – annual OPEX breakdown of solvent management options*

As would be expected, solvent losses dominate for those techniques requiring complete solvent replacement on reaching the fully used condition. Water and waste costs are minimal compared to the raw solvent. By design thermal reclaiming significantly reduce solvent losses, however the maintenance of the thermal reclaimer equipment, significant consumption of sodium hydroxide and cost of specialist waste treatment negate these benefits for MEA. For ion exchange, in addition to caustic usage, the cost of waste and the regular replacement of resin dictate annual expenditure. For the preventative methods nitrogen makes up the next highest contribution to cost for DORA but is the primary operating cost for nitrogen sparging (based on 0.1 wt% of flue gas). Membrane replacement costs constitute ~6% of total OPEX for DORA.

Changing to a CESAR1 process realises lower quantities of solvent, water and waste associated with a lower inventory and threshold, but ~4x higher solvent costs drive the total annual operating costs higher than for MEA. Conversely, thermal reclaim and ion exchange, which are not so dependent on solvent price, become most cost effective. The annual operating cost for DORA upstream, which was higher than baseline for MEA, is also seen to be lower for CESAR1, through a 25% reduction in solvent costs.

Moving from 90 to 95% capture sees a near proportional increase in O&M for all techniques with the exception of thermal reclaim and ion exchange.

Figures 16 to 18 graph total cost versus plant operational lifetime for the individual corrective and preventative solvent management options for PC cases 1 to 3.

For the MEA plant, the optimal continuous bleed and feed level amounts to 0.08% of the total inventory mass per day. Although thermal reclaim has a slightly lower gradient than the baseline the high total plant cost does not allow for breakeven over the 36 years operation. On the other hand the ongoing costs for ion exchange diverge from the baseline. None of the preventative techniques comes close to the baseline. Despite a similar plant cost in its current form nitrogen sparging would lead to approximately triple the total outlay compared to regularly replacing the spent solvent.

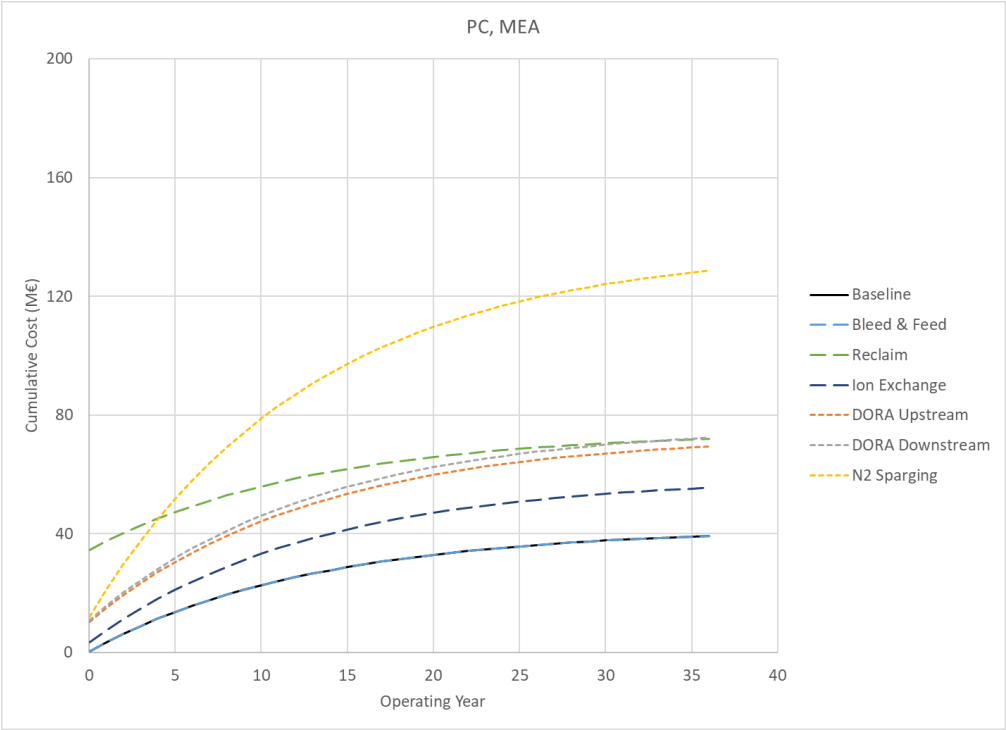


Figure 16 *PC plant base case 1 - cumulative total cost versus time for solvent management options*

For the CESAR1 plant, bleed and feed rate decreases to 0.05% of the total solvent inventory due to the higher capacity of the solvent. The higher cost of solvent means that thermal reclaiming repays investment after seven years. However, ion exchange is the most cost-effective method of treatment. Over the entire operating life the selection of DORA upstream of the absorber sump comes close to being viable. DORA downstream and nitrogen sparging remain more costly.

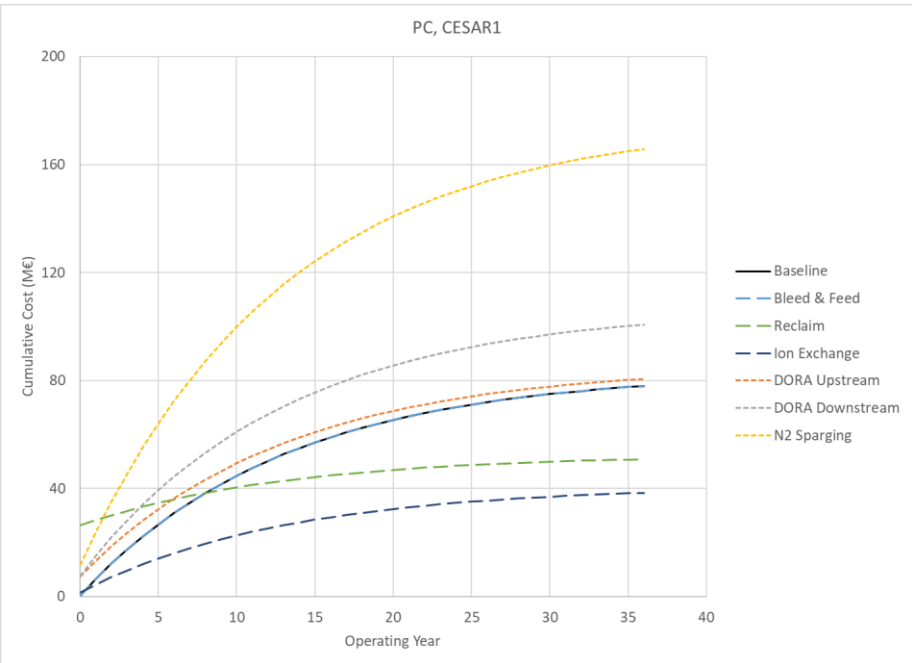


Figure 17 *PC plant base case 2 - cumulative total cost versus time for solvent management options*

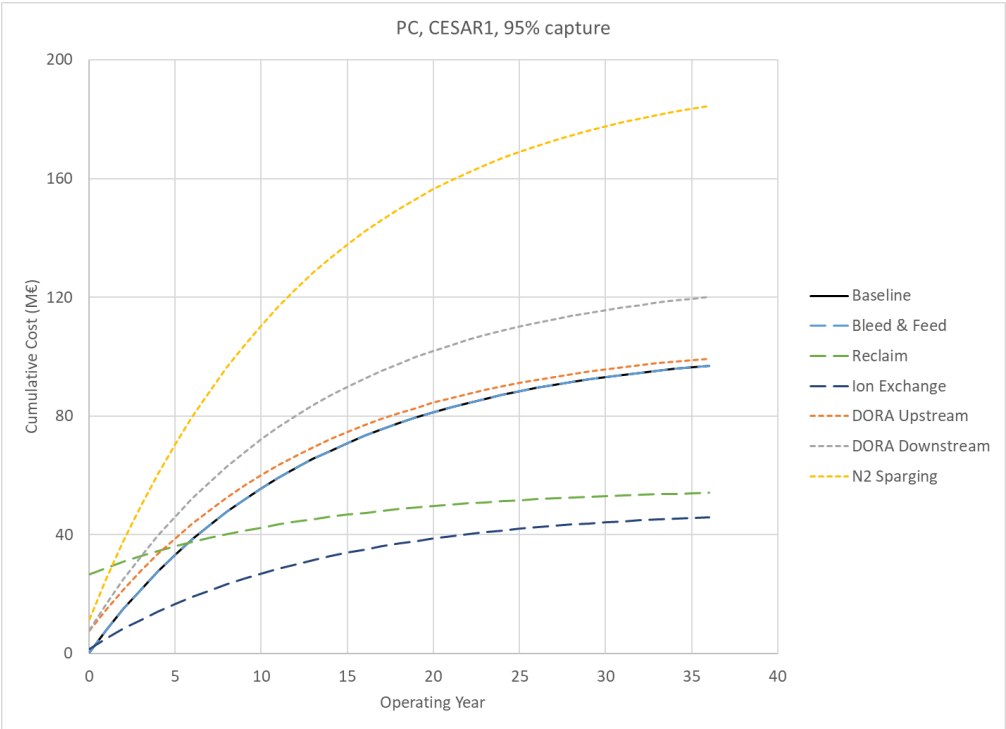


Figure 18 *PC plant base case 3 - cumulative total cost versus time for solvent management options*

With the plant designed for increasing capture rate the cost of the baseline increases and the continuous bleed and feed rate amounts to 0.2% of the solvent inventory. The relative savings possible through ion exchange and thermal reclaiming become greater still, although the cost of the preventative techniques generally remain prohibitive.

6.3.5 EfW plant baseline costs

Incremental capital and operating costs with no active solvent management other than particulate filter on the two EfW plant cases are given in Table 11.

Table 11 *EfW plant base cases 4 and 5 summary results*

EfW case	PCC plant	4	PCC plant	5
Solvent	MEA		CESAR1	
Carbon capture (%)	90		90	
Total plant cost (M€)	19.9	0.05	20.5	0.04
Fixed OPEX (M€/yr)	1.3	0.002	1.4	0.002
Variable OPEX (M€/yr)	3.3	0.43	2.6	0.80
Total OPEX (M€/yr)	4.6	0.44	4.1	0.80
Capture cost (M€/tCO_2)	36.6	1.4 (4%)	34.8	2.6 (7%)

The frequent replacement of solvent in the EfW plant - two to three months - corresponds to high annual variable operating costs, which increases the baseline capture costs significantly. From the previous study [6], assuming 200 days for MEA and 400 days for CESAR1 the comparable figures were 0.6 (+2%) and 1.1 M€/tCO_2 (+3%). However, that analysis made a separate allowance for ongoing solvent make-up due to emissions, which brings the total from the two methods into alignment, albeit for differing degradation rates.

6.3.6 EfW plant solvent management costs

Figure 19 presents the comparison of total capital and operating costs for the individual corrective and preventative solvent management options for EfW cases 4 (MEA) and 5 (CESAR1). These follow similar trends to the PC plant.

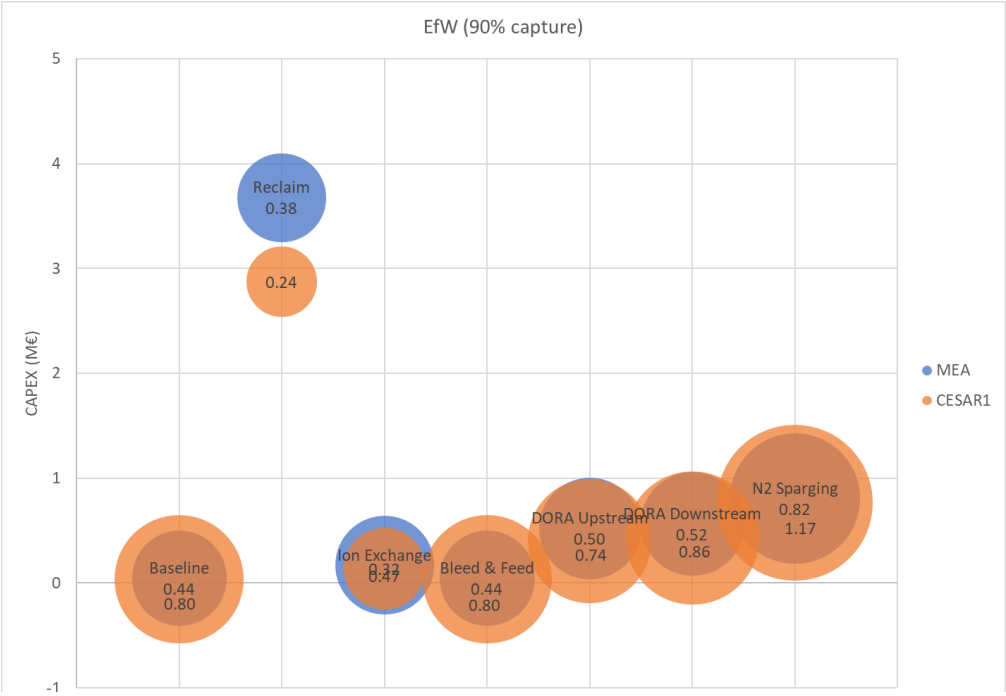


Figure 19 *EfW plant base cases 4 and 5 – total plant cost and OPEX of individual solvent management options*

Figures 20 and 21 present the breakdown of annual operating costs for the individual corrective and preventative solvent management options for EfW cases 4 and 5.

Akin to the PC case solvent costs dominate but proportionally more so as result of the reduced time to replacement. On the other hand the higher degradation rates increase the frequency of treatment by thermal reclaim and ion exchange. For MEA, these increases are of a similar magnitude whereas for CESAR1 solvent costs dominate.

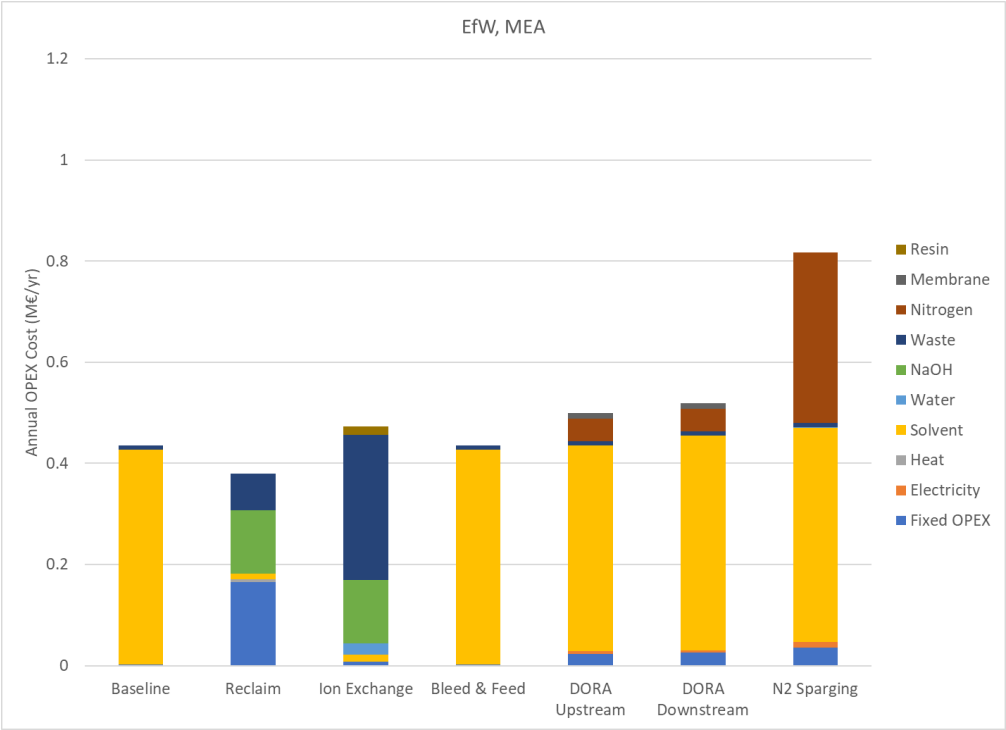


Figure 20 *EfW plant base case 4 – annual OPEX breakdown of solvent management options*

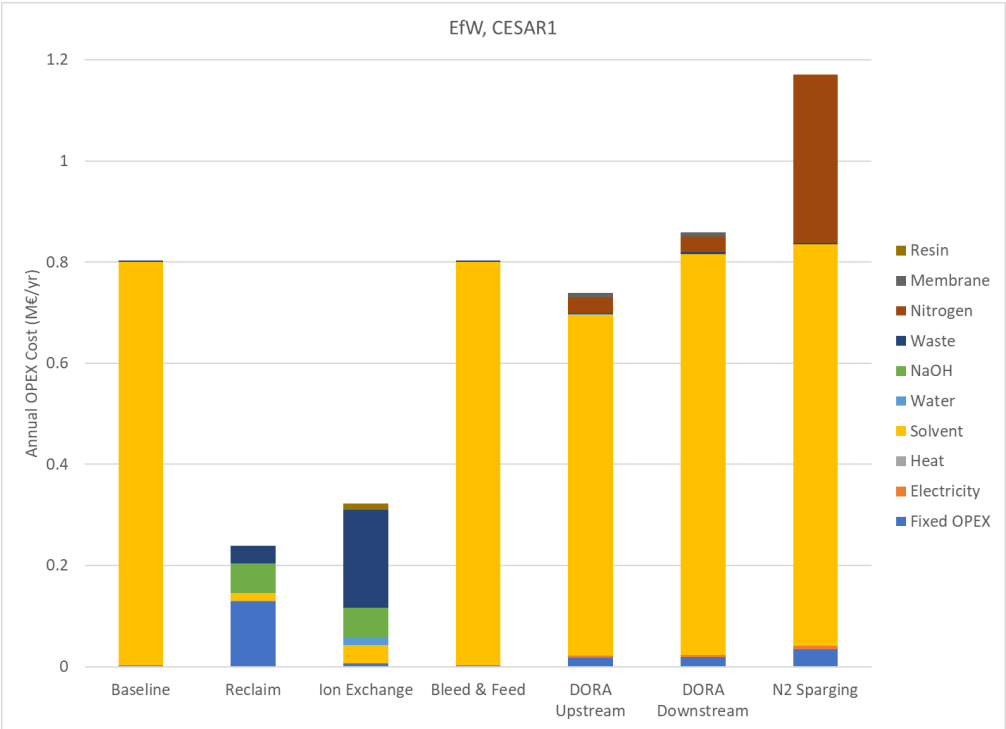


Figure 21 *EfW plant base case 5 – annual OPEX breakdown of solvent management options*

Figures 22 and 23 graph total cost versus plant operational lifetime for the individual corrective and preventative solvent management options for EfW cases 4 and 5.

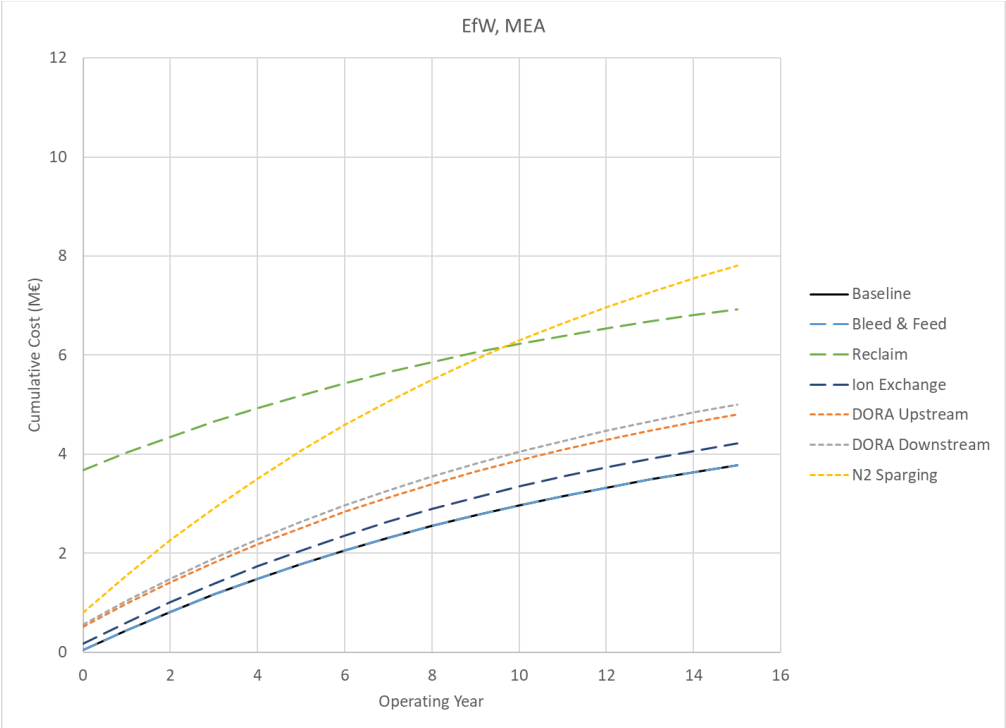


Figure 22 *EfW plant base case 4 - cumulative total cost versus time for solvent management options*

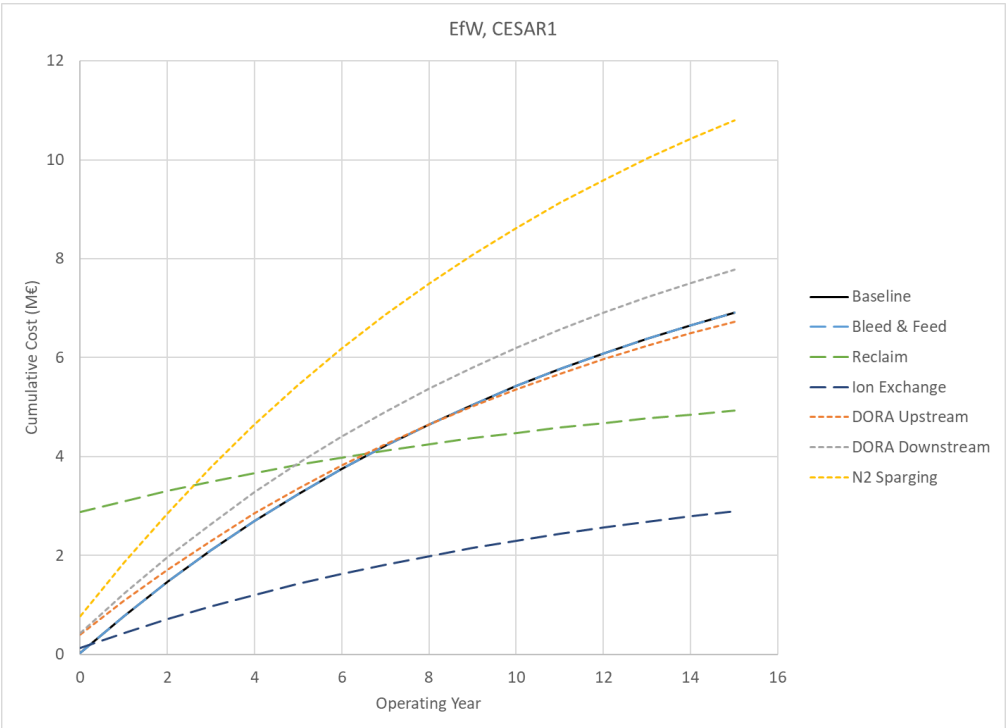


Figure 23 *EfW plant base case 5 - cumulative total cost versus time for solvent management options*

Again, no technique - beyond an optimisation of bleed and feed (0.72 and 0.37% inventory per day for MEA and CESAR1, respectively, for continuous option) - provides a more cost-effective means than regular

replacement of the MEA inventory. For the CESAR1 solvent thermal reclaim and, particularly, ion exchange may be able to realise significant cost savings over the limited lifetime of the EfW plant. DORA is seen to breakeven after eight years.

6.3.7 CCGT plant baseline costs

Incremental capital and operating costs with no active solvent management other than particulate filter on the CCGT plant case are given in Table 12.

Table 12 *CCGT plant base case 6 summary results*

CCGT case	PCC plant	6
Solvent	MEA	
Carbon capture (%)	85	
Total plant cost (M€)	463	0.2
Fixed OPEX (M€/yr)	9.5	0.01
Variable OPEX (M€/yr)	8.4	5.17
Total OPEX (M€/yr)	17.9	5.18
Capture cost (M€/tCO_2)	85.9	4.6 (5%)

As noted in Section 2.2.3 the CCGT PCC plant only capture cost is skewed by the finance of a longer-term capital investment. Despite this, however, a higher flue gas oxygen means that the baseline solvent management cost of carbon captured still amounts to 5% of the PCC plant cost.

6.3.8 CCGT plant solvent management costs

Figure 24 presents the comparison of total capital and operating costs for the individual corrective and preventative solvent management options for CCGT case 6 (MEA).

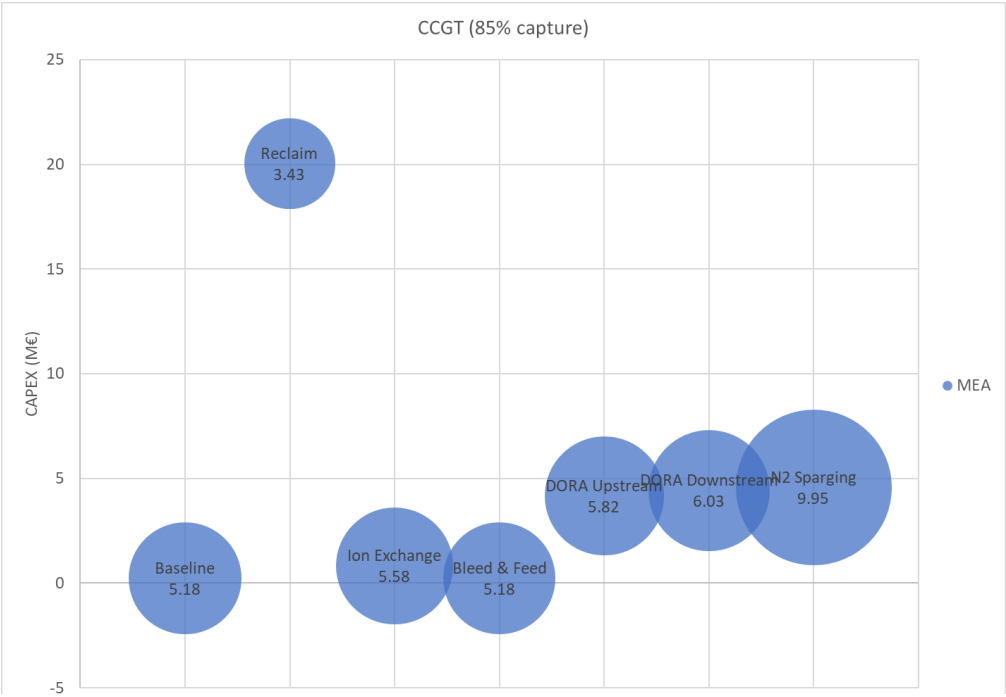


Figure 24 *CCGT plant base case 6 - total plant cost and OPEX of solvent management options*

Figure 25 presents the breakdown of annual operating costs for the individual corrective and preventative solvent management options for the CCGT case.

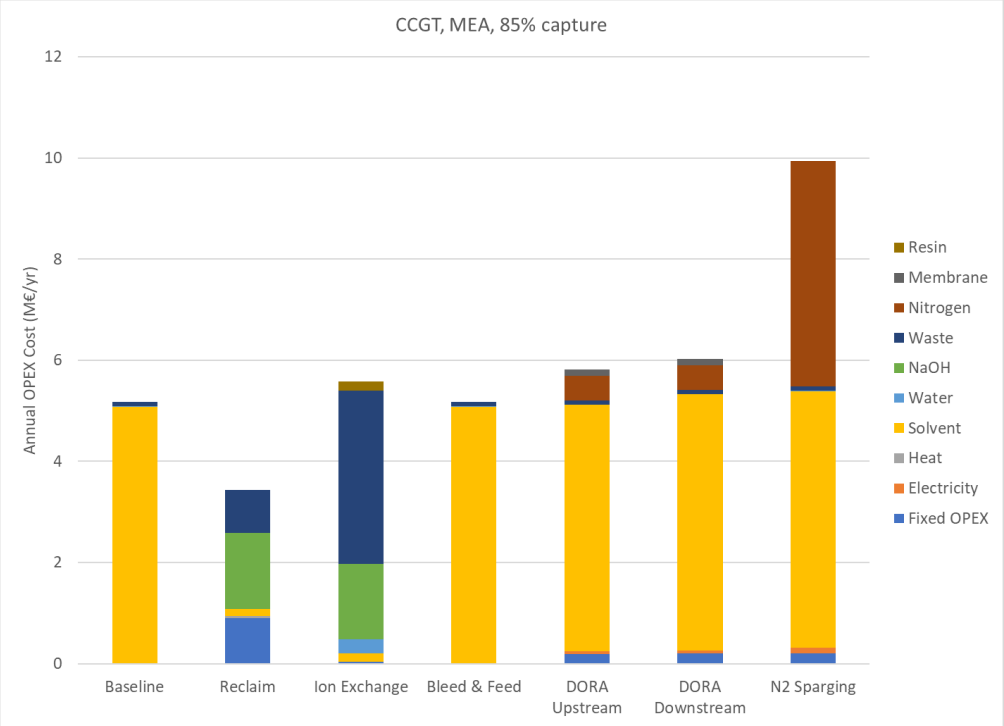


Figure 25 *CCGT plant base case 6 - annual OPEX breakdown of solvent management options*

As with the EfW plant the very high degradation rate combined with the scale of the CCGT case corresponds to a high annual OPEX, primarily because of solvent cost. As such, thermal reclaim becomes more advantageous due to a lower quantity of waste produced.

Figure 26 graphs total cost versus plant operational lifetime for the individual corrective and preventative solvent management options for the CCGT case.

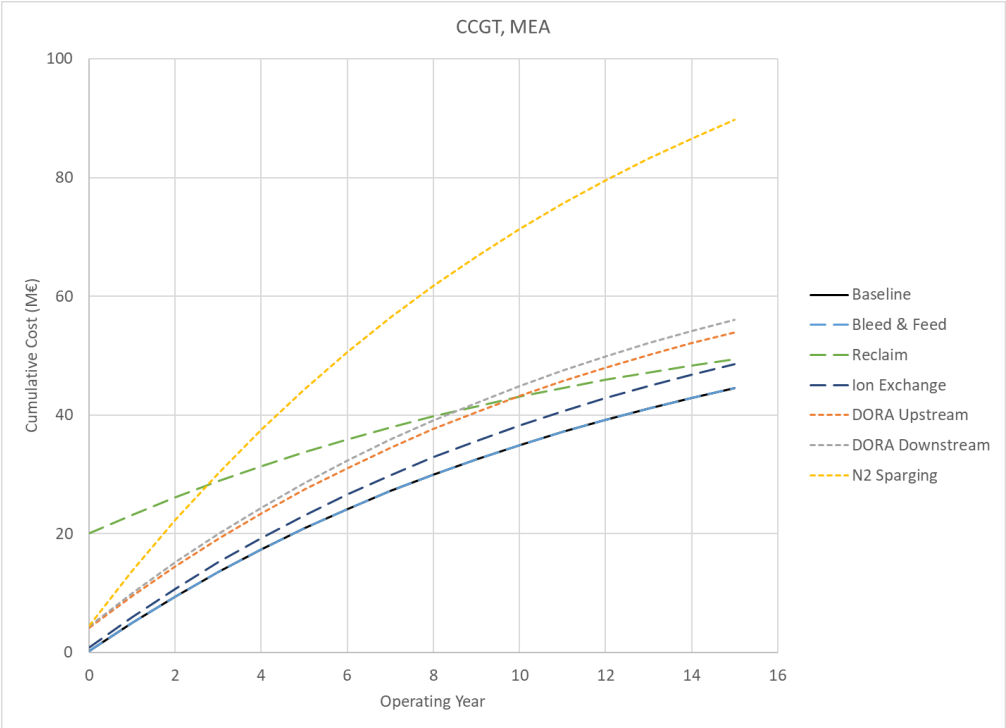


Figure 26 *CCGT plant base case 6 - cumulative total cost versus time for solvent management options*

The optimal continuous bleed and feed level amounts to 0.71% of the total inventory, in line with the EfW plant figure. Contrary to the PC and EfW plant with MEA solvent, thermal reclaim comes closer to breaking even on the CCGT plant due to a high degradation rate on a large-scale plant. The sensitivity to an increased capture rate of 95% is discussed in Section 7.

6.4 Case summary

A summary of the costs associated with the baseline and the preferred solvent management techniques for each case is given in Table 13.

Table 13 *Summary of baseline and preferred solvent management techniques*

Case	1		2		3		4		5		6	
Plant	PC		PC		PC		EfW		EfW		CCGT	
Solvent	MEA		CESAR1		CESAR1		MEA		CESAR1		MEA	
Carbon capture (%)	90		90		95		90		90		85	
Solvent Management	Base	BF	Base	IE	Base	IE	Base	BF	Base	IE	Base	BF
Total plant cost (M€)	489	-	405	407	382	384	19.9	-	20.5	20.6	463	-
Fixed OPEX (M€/yr)	24.0	-	20.0	20.1	19.0	19.1	1.3	-	1.4	1.4	9.5	-
Variable OPEX (M€/yr)	4.3	≤	9.6	6.1	12.2	7.7	3.7	≤	3.4	2.9	13.6	≤
Total OPEX (M€/yr)	28.3	≤	29.6	26.2	31.2	26.8	5.0	≤	4.9	4.3	23.1	≤
Capture cost (M€/tCO_2)	31.8	≤	27.3	27.1	26.9	26.6	38.0	≤	37.4	35.9	90.5	≤
Cost increase (%)	1	≤1	2	1	2	1	4	≤4	7	3	5	≤5

Whilst bleed and feed is preferred for MEA due to its relatively low cost, the corrective options of ion exchange - and to a good extent thermal reclaiming - become cost-effective for the more expensive CESAR1 solvent.

With the exception of DORA (upstream) on the EfW plant with CESAR1 the preventative techniques are currently not able to better the regular replacement of the spent solvent on a cost basis.

As illustrated by Figure 27, such are the additive costs versus the marginal benefit of the preventative options, the combination of techniques is not seen to be cost-effective.

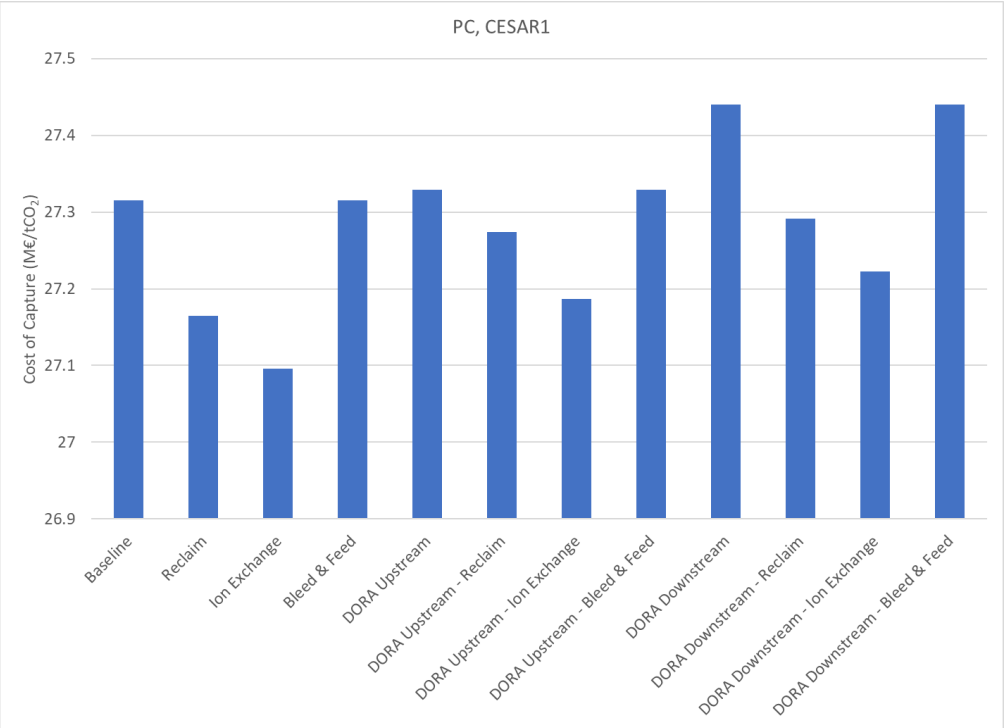


Figure 27 *PC plant base case 2 - capture cost for solvent management combinations*

7 Sensitivity study

7.1.1 MEA solvent cost

Alongside degradation rate it is clear from the results that the unit cost of solvent is a very important gauge of cost-competitiveness. Considering the limited solvent management options available to the MEA plant, a sensitivity was carried out to the increase in this parameter necessary to bring another technique (ion exchange) into contention. This is illustrated for the PC plant in Figure 28.

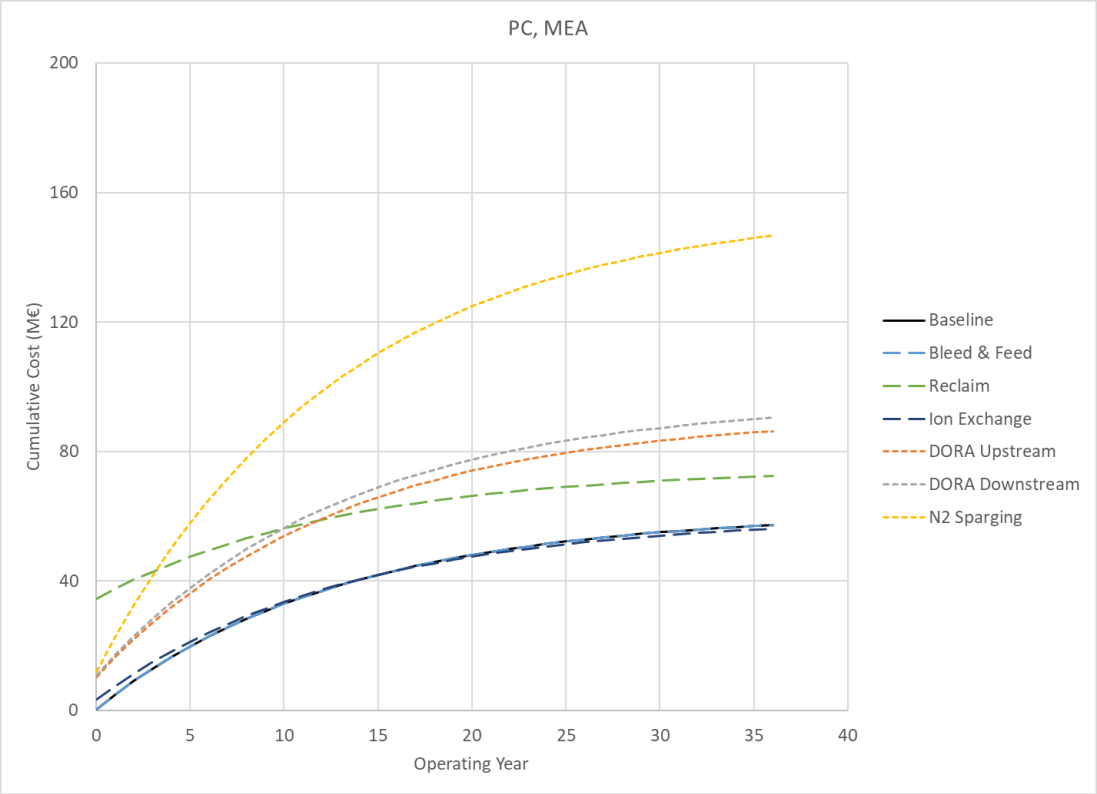


Figure 28 *PC plant base case 1 - cumulative total cost versus time for solvent management options with MEA unit cost 3,100 €/t*

Table 14 presents approximate MEA unit cost escalation required for the breakeven of ion exchange (ion exchange or thermal reclaim in the CCGT case) as economically viable on the selected plant. Whilst a notable increase would be needed for the PC plant, the very high solvent wastage rate on the other plant means that a more plausible 14-19% increase in unit cost could be sufficient to breakeven in the 15 years lifespan considered.

Table 14 *MEA cost for breakeven of ion exchange as a viable solvent management technique*

Case	1	4	6
Plant	PC	EfW	CCGT
Carbon capture (%)	90	90	85
Availability (%)	85	90	57
Approximate breakeven MEA unit cost for ion exchange (€/t)	3,100 (+48%)	2,400 (+14%)	2,500 (+19%)

7.1.2 CCGT plant at 95% capture

Using available input from a 95% capture design for the CCGT plant, the results presented in Table 15 were produced. Note that in the absence of a reference PCC plant only cost, the cost increase for solvent management has been calculated relative to the 85% figures.

Table 15 *CCGT plant summary results (MEA solvent)*

Case	PCC plant	6	6 (TR)	7	7 (TR)
Carbon capture (%)	85			95	
Degrade rate (g/tCO_2)	1510			1541	
Time to threshold (days)	57			56	
Total plant cost (M€)	463	463	483	463	483
Fixed OPEX (M€/yr)	9.5	9.5	10.4	9.5	10.4
Variable OPEX (M€/yr)	8.4	13.6	10.9	14.3	11.3
Total OPEX (M€/yr)	17.9	23.1	21.3	23.8	21.7
Capture cost (M€/tCO_2)	85.9	90.5 (5%)	91.0 (6%)	91.1 (6%)	91.3 (6%)

Figure 29 graphs total cost versus plant operational lifetime for the baseline and thermal reclaimer solvent management options for the CCGT case. This further illustrates the relative gain to be had from increasing the capture rate to 95%, with thermal reclaim for case 7 almost breaking even. A higher plant availability may be expected to ensure a cost benefit within the 15 years' operating life.

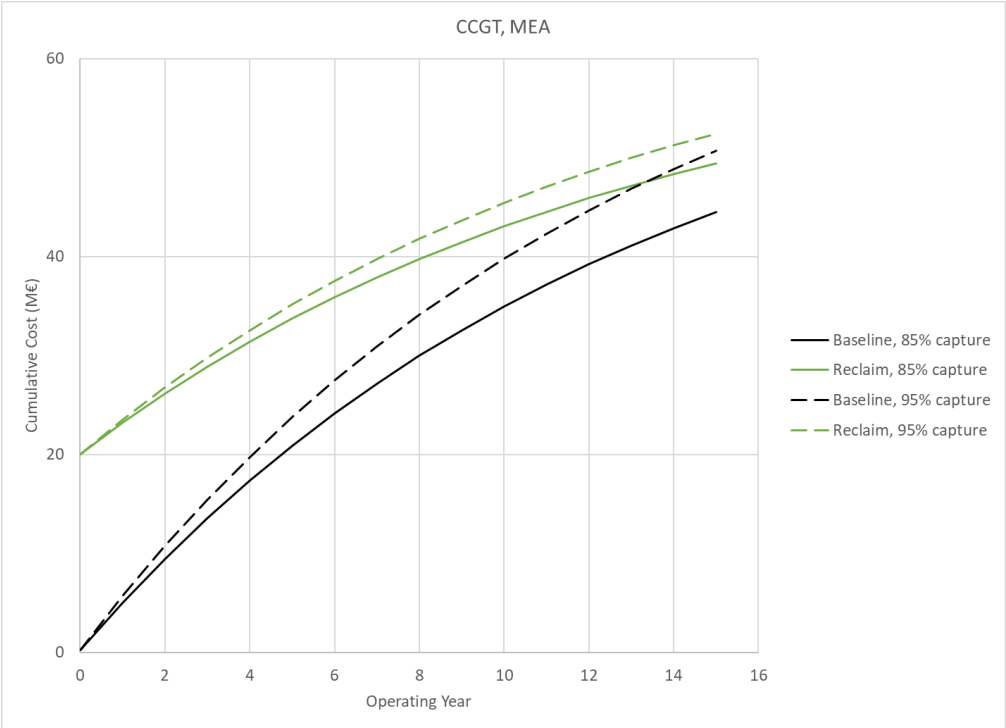


Figure 29 *CCGT plant base cases 6 and 7 – cumulative total cost versus time for solvent management options*

8 Guidelines for solvent management

It is caveated that there are a number of limitations and uncertainties in the technical and economic calculations applied. Therefore, the following guidelines should be treated as indicative only. The degradation model used as basis for the calculations has been described in D1.3.4, and in there a full description of the current model limitations is given. This TEA exercise should be repeated once an updated version of the model is available.

The results of this activity point to solvent management preferences that are highly dependent on solvent:

- MEA: Bleed and feed, with potential for thermal reclaim on CCGT plant
- CESAR1 (PC and EfW plant only): Ion exchange > thermal reclaim > bleed and feed

For any solvent the use of a lower bleed and feed rate during the initial period of operation (i.e. allowing an underlying level of degradation products to accrete) may generate some savings. The cost benefits to such an approach would be compounded for an advanced solvent carrying higher unit cost. However, the characteristics of solvent degradation particular to the specific plant will be required to be known for monitoring and use of bleed and feed to be successful. This is especially true for MEA, which displays a self-accelerating degradation trend that cannot be easily rectified.

The potential of ion exchange (combined anionic and cationic) is in line with RWE's experience on their Niederaussem pilot, although it is commented that applying no corrective treatment at all is the current best practice for CESAR1, both in terms of managing the solvent condition and minimising waste [11]. As such, the typical guidance provided at present [20] [21] to try and keep the solvent as clean as possible may not be entirely applicable for second or third generation solvents. In any case, however, a particulate filter should be used to minimise emissions.

It is recognised that solvent management must be considered in the context of the total lifecycle of chemicals and energy usage in production, transport and waste of the solvent, and not least, permitting laws in the future. In addition, effective solvent management has operational benefits, reducing the potential for system upsets, such as foaming, which can lead to plant downtime and increased emissions through the stack. Therefore, operating philosophies and technologies to reduce oxidative and thermal degradation should be the front line of solvent management. The use of techniques to reduce dissolved oxygen at the absorber sump and downstream show potential to be cost-effective in this regard.

The DORA and N_2 sparging technologies are still under development. The results of this TEA are a direct consequence of the degradation network model predicting that most of the degradation happens in the absorber packing, for both MEA and CESAR1. Contrary to what the model predicts, pre-piloting results (TRL5) indicate that DORA has a positive impact in lowering the degradation rate of MEA. An updated version of the degradation model and further piloting data on both DORA and N_2 sparging may confirm those earlier results. The current analysis show that, for N_2 sparging, the main focus should be on lowering the N_2 flowrate required.

For thermal reclaiming, the main cost factor is the CAPEX. Improving the design of the unit so that the CAPEX could be lowered could be an option. An alternative to that, and already in use by the oil and gas industry, is to have thermal reclaiming as a service. In that case, a third company owns a mobile thermal reclaimer unit, and operates at regular intervals on different plants. While a service fee is included in the costs, the investment is diluted over multiple players. This option could definitely improve the feasibility of thermal reclaiming.

9 Conclusions

ALTRAD has successfully developed a software tool to perform techno-economic calculations on different solvent management strategies, which allows to incorporate solvent degradation models to the design and assessment of solvent management technologies. The tool results reflect the different model assumptions. While the extensive campaigns of MEA (ALIGN) and CESAR1 (ALIGN and LAUNCH), including tests with different solvent management technologies, have greatly informed the current models, knowledge gaps remain that influence the conclusions.

This study is a clear first attempt in quantifying the effect of different solvent management strategies for different types of industries that are implementing carbon capture technology. While a fully functioning software tool is created, the results are very dependent on the input data, for which a lot of uncertainties are currently still present. Additionally, the tool has shortcomings regarding the calculation method and the implementation of the different solvent management technologies, which can be improved in a next version. Nevertheless, the tools generates initial insights in the effectiveness of several solvent management strategies, on which the carbon capture community can built their future endeavours towards researching and evaluating solvent management strategies. It also gives clear indications regarding future steps in the current models and technology developments, including the need to lower the nitrogen consumption for nitrogen sparging, evaluation of CAPEX saving strategies for thermal reclaiming (e.g., use of mobile rental units), and the relevance of degradation models for the evaluation of oxygen removal technologies.

Conclusions on solvent management for MEA

For thermal reclaiming, the study indicates that this technology cannot be cost competitive with the baseline case for any use case. The main cost driver of thermal reclaiming comes from the CAPEX of the thermal reclaimer. This could be mitigated, if thermal reclaimers could be offered on a rental agreement basis, as companies only need these units to be on site at times when reclaiming is performed (typically a few weeks per year). It has to be noted that no thermal reclaiming tests were performed within LAUNCH, and there are knowledge gaps that prevent a very comprehensive analysis of this technology. As an example, the avoided downtime for solvent replacement/troubleshooting by using a thermal reclaimer is not taken into account, as it could not be properly quantified. This, however, is known to be a major economic benefit of reclaiming. Next to economic factors, also ecological factors play a role. To this extend, thermal reclaiming could greatly reduce disposal of solvent. A more detailed analysis of thermal reclaiming is required to draw further conclusions on the effectiveness of thermal reclaiming for MEA systems (and solvent systems in general). A similar conclusion can be drawn for ion-exchange reclaiming. However, since the CAPEX investment for this technology is expected to be lower (while having similar efficiency), it gives better results than thermal reclaiming. Also here, more detailed analysis of the technology is required.

The oxygen removal technologies show relatively bad results for the MEA processes, as the vast majority of the oxidative degradation (94%) is calculated to be occurring in the absorber packing, where the oxygen removal technologies have no effect on. The OPEX numbers for DORA are consistently higher than the baseline case, indicating that in this specific case, the technology does not lead to a positive business case. For nitrogen sparging, the high nitrogen consumption leads to a worse business case, indicating that this specific technology needs to reduce its nitrogen usage before it can be considered against other technologies on a commercial scale. As stated above, more research is needed towards the division of degradation between the absorber packing, sump and lean/rich HEX before further conclusions can be drawn on the effectiveness of oxygen removal technologies for MEA systems. Once a new, extended version of the degradation model is available, it can be implemented in the tool for re-evaluation of these technologies.

Conclusions on solvent management for CESAR1

For thermal reclaiming, the study indicates that this technology can be competitive to the baseline, as the OPEX for reclaiming is much lower than exchanging the solvent. This is mainly due to the high costs of the solvent (as compared to MEA), which are mitigated by reclaiming the solvent. While the CAPEX of the reclaimer still causes a high initial investment, breakeven point between 5 to 8 years can be expected. Similar to MEA, this is still excluding potential other cost savings of reclaiming, like reduced downtime of the plant and shared/rental equipment. The ion-exchange gives even better results (breakeven point below 1 year), due to the lower initial investment and similar efficiency compared to thermal reclaiming. To determine a more

accurate potential of thermal reclaiming and ion-exchange reclaiming for CESAR1, a more detailed case study is necessary to draw further conclusions on feasibility.

Regarding oxygen removal, the calculated degradation split between the absorber packing, absorber sump and lean/rich heat exchanger (70/28/2%) determine the efficiency of oxygen removal technologies. With 98% of the oxidative degradation occurring before the lean/rich heat exchanger, the downstream (of the absorber sump) oxygen removal technologies do not generate a positive business case, as the amount of degradation that can be prevented is limited. For the upstream (of the absorber sump) configuration, the DORA oxygen removal technology shows slightly lower OPEX than the baseline, with total costs similar to the baseline case to due to initial CAPEX investment required for this technology. Again for nitrogen sparging, the nitrogen demand generates high costs for this case, hindering a positive business case. As mentioned before, if the division of the degradation between the different part of the process if different than calculated in this report, this could have a direct effect on the estimated effectiveness of oxygen removal technologies. A lower fraction of degradation in the absorber packing and sump would have a direct positive effect in the evaluation of the oxygen removal technologies installed upstream and downstream of the absorber sump. Further analysis is required to assess the full potential of the oxygen removal technologies for CESAR1.

10 Recommendations for further work

The recommendations for further work arising from this activity can be categorised into degradation calculation, full-scale techno-economic modelling and solvent management optimisation.

The following recommendations relate to degradation modelling:

- The oxidative degradation network model for both MEA and CESAR1 should be improved. The limitations of the current model are extensively discussed in D1.3.4
- The oxidative degradation network model could be extended to cover other solvents of interest
- A similar thermal degradation model could be created based on stripper process conditions.

With respect to techno-economic calculation, it is recommended that:

- Losses to solvent degradation and those to emissions be treated separately in order to quantify the division between ongoing solvent make-up and replacement. Alternatively solvent wastage could be calculated considering the accumulation of degradation products in the solvent.
- The rich pipework to and from the cross heat exchanger be incorporated for oxidative degradation
- Further validation be carried out of total degradation rate to pilot or full-scale plant across a range of flue gases and operating conditions for different solvents
- Equipment sizing, as well as bottom-up costing, are better developed to improve estimate class
- A lifecycle assessment approach is considered to include the CO_2 impact of solvent management options – particularly those which require significant amounts of fresh solvent and create large solvent waste streams such as bleed and feed.

Regarding preventative solvent management, the following points are recommended:

- The potential shown by DORA for the CESAR1 solvent may be realisable in future through process optimisation and supply chain economies of scale. This could consider how to generate less oxidation in the absorber for chemicals and utilities reduction as well as the integration of the column into the existing plant
- A reduction in the nitrogen requirement would also greatly assist the cost effectiveness of nitrogen sparging, which could present a simpler solution for implementation of dissolved oxygen reduction
- Other measures to reduce degradation, such as iron or nitric oxides reduction, should be included where experimental data substantiates it.

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