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

Deliverable Nr. 5.2.2/3

Controlling degradation: the impact of iron and impurities removal on the degradation of CO₂ capture solvents

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Executive summary

The impact of the removal of iron and impurities on the degradation of CESAR1 by applying solvent management technologies with different effect mechanisms (adsorptive removal, ion exchange) was investigated and checked against each other in a unique 41 months (1,240 days or 29,760 testing hours) long-time test at the CO₂ capture plant at Niederaussem without solvent inventory exchange and almost continuous 24/7 operation. The testing program comprised:

- operation without any solvent management technology (216 days no active carbon or particle filters in use)
- operation without active carbon filter (in total 739 days) and operation of the filter with two different active carbon qualities (active carbon A 471 days and active carbon B 30 days, in total 501 days)
- ion exchange using an anion exchange resin (within 75 days solvent inventory treated two times)
- serial configuration of cation and anion exchange resins (114 days, inventory treated four times).

The results of the test campaign of solvent management technologies with CESAR1 are contrary to the general recommendations according to an inappropriate guideline from the UK Environment Agency (published in July 2021) on best available technologies and some tests with 30% MEA which have been short compared to the time-scale of solvent degradation. The BAT document must be revised.

Main results are:

- Dependent on the active carbon properties, solvent treatment by adsorptive removal of colouring agents - which are formed during the aging of the solvent - can reduce the visible absorbance of the solvent. One of the two tested active carbon qualities could also reduce the iron and chloride concentration, but this has no significant effect on the solvent degradation rate and performance of CESAR1. The colour of the solvent is an inappropriate parameter to control/activate solvent management technologies.
- One of the two tested active carbon qualities caused a significant increase of the foaming tendency of the solvent and required an increase of the dosing of antifoaming agent by a factor of 20.
- A significant part of the dissolved iron (and also zink and chromium) forms negative charged complexes.
- The concentration of iron and other metals in the solvent does not necessary correlate with the degradation rate of CESAR1.
- Anionic compounds, trace components and metal complexes can be effectively removed from the solvent by ion exchange using an anionic exchange resin (removal of >50% after treating the solvent inventory two times, >80% after treating the inventory four times), but removal of anions alone causes a significant increase of the degradation of CESAR1 by a factor of two.
- Cations can effectively be removed from the solvent by a cationic exchange resin (70-100% after treating the solvent inventory four times), but this did not reduce the degradation rate compared to sole application of anionic exchange.
- In contrast to MEA, also a significant part of the uncalibrated components (contaminants which are detected in the analysis by gas chromatography, but which cannot be assigned to specific compounds) can be removed from the solvent by ion exchange.
- Removal of all contaminants from CESAR1 as fast as they are formed (according to the requirements from the UK Environment Agency) is contra-productive and would cause unnecessary waste of solvent and resources, efficiency losses as well as the unnecessary generation of wastes.



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1 Introduction

Recently, a guidance was published by the UK Environment Agency that proposes “best available techniques” which should be the optimum for preventing or minimising emissions and impacts on the environment from post-combustion carbon dioxide capture at power plants [1]. According to this, solvent management is a very important factor for the environmental footprint of amine-based CO₂ capture. It is required that:

- amine-based solvents should generally be clear and transparent,
- “significant” changes of the solvent colour should automatically require the application of reclaiming,
- all non-solvent constituents should be removed from the solvent inventory as fast as they are added during operation to avoid their accumulation.

This guidance follows the many times heard mantra of solvent degradation management in amine-based post combustion capture “keep the solvent clean” to minimise solvent consumption. The underlying idea tries to connect increasing corrosivity of the solvent with increasing concentration of organic acid residues formed by amine oxidation that results in increased release of metal ions from the capture plant components into the solvent which act together with degradation products as catalysts for the amine degradation. It is assumed that the amine losses would decrease by the removal of metals, degradation products and accumulated trace components which are captured from the flue gas.

To a large extent the experimental basis for the underlying assumptions and recommendations is limited to simplified laboratory experiments or testing campaigns at pilot plants which are short compared to the time-scale of solvent degradation processes, and are related to the solvent 30 wt.% aqueous monoethanolamine (MEA) only [2]. So, derived from tests at the Technology Center Mongstad with MEA, some authors proposed colour as a degradation indication, suggest “transparent” as a threshold value, and recommend reclaiming in case of any significant colour change. Additional degradation indicators and threshold values include: ammonia emission (5 ppmv), heat stable salts (1.5 wt.% of the amine as HSS), metals (5 ppmv), and the sum of degradation products concentration (3 wt.%). Reclaiming is suggested in case any of these variables achieve the threshold limit.

However, this theoretical hypothesis disregards the complexity of the solvent matrix, interaction of potential catalysts of the amine degradation reactions with degradation products – namely metal complexes – and oxidizing agents, and specific requirements which must be fulfilled before a degradation mechanism can proceed. In laboratory experiments quite often drastic artificial parameters regarding partial pressure of gaseous components, temperatures, and concentrations of components in the solvent, are applied to reduce the testing time and in the hope to achieve strong and conclusive effects.

It is important to evaluate the effect of the proposed solvent management approaches and the hypotheses about solvent degradation based on results from real long-time pilot plant or full-scale tests using fully representative, industrial flue gases to avoid waste streams and efficiency losses that may result from contra-productive overshooting efforts for solvent management. The consequences of the proposed guiding principles are directly connected with the economics of amine-based CO₂ capture, conflicting environmental goals due to cross-media effects (management of solvent consumption, decreased energetic efficiency, generation of waste-streams) and consequences for the permitting, operation and implementation of CO₂ capture plants.

The results presented in this deliverable contribute to correct the proposed guidance principles and to maximise the environmental benefit of amine-based post-combustion capture for an accelerated implementation of CO₂ capture. Additionally, especially the results of the ion exchange campaign provide a new impetus for more focused investigations on the interaction of metal cations, which have the potential to act as a catalyst for oxygen activation and solvent degradation, and degradation products with capability to form complexes to avoid the opposite of the expected effect when activating solvent management technologies. An intelligent combination of complementary laboratory experiments - making also use of solvent from real operation - with meaningful pilot plant tests of sufficient duration and innovative approaches like the head-to-head operation of CO₂ capture plants of different size realized in LAUNCH, offer the opportunity to clarify the effects caused by the interventions of solvent management and effective key factors for solvent degradation in industrial CO₂ capture.



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This deliverable unites the initial deliverables on the impacts of ion-exchange-based reclaiming (D5.2.2) and adsorption of trace elements in the solvent on degradation of CEASR 1 (D5.2.3) to directly compare the effects of the solvent management technologies.

2 Capture pilot plant at Niederaussem and test of solvent management

2.1 Capture pilot plant at Niederaussem and boundary conditions

The post-combustion capture pilot plant at Niederaussem was commissioned in 2009 and has meanwhile an accumulated operating time of more than 100,000 hours. It is operated in a 24/7 mode (three shifts per day) by the R&D operating team of RWE Power. The capture capacity is up to 7.2 t of CO₂ per day at a flue gas flow of 1,550 kg/h. Typical concentrations in the flue gas at the absorber inlet are: CO₂ 15.2 vol.-%, dry, O₂ 5.5 vol.-%, dry, SO₂ <1 mg/m³, dry (STP); dust <1 mg/m³, dry (STP); NO_x 100 – 160 mg/m³, dry (STP), NO₂ 2 - 8 mg/m³, dry (STP), see Table 1.

Table 1. Typical operating parameters and boundary conditions during the testing campaign with CESAR1 at Niederaussem (STP - standard temperature and pressure: 273.15 K and 101.325 kPa; dry, 6% O₂ correction).

Parameter	Unit	
Flue gas temperature at DCC inlet	°C	64
Flue gas temperature at absorber inlet	°C	40 – 45
Flue gas flow	m ³ /h, dry (STP)	1150
CO ₂ content of the flue gas at absorber inlet	vol.%;dry	15.2
O ₂ content of the flue gas after desulfurization	vol.%;dry	5.5
SO ₂ content of the flue gas before desulfurization	mg/m ³ , dry (STP)	1000 – 3000
SO ₂ content of the flue gas before DCC	mg/m ³ , dry (STP)	60 – 160
SO ₂ content of flue gas at absorber inlet	mg/m ³ , dry (STP)	<1
Dust content of the flue gas before DCC	mg/m ³ , dry (STP)	<2
NO _x content of flue gas at absorber inlet	mg/m ³ , dry (STP)	100 – 160
NO ₂ content of flue gas at absorber inlet	mg/m ³ , dry	2 – 8
Solvent flow rate	kg/h	2600-3100
Water circulation in the DCC	kg/h	8000
pH value of water in the DCC	-	7 – 7.2
CO ₂ -lean flue gas temperature at water wash outlet	°C	40 – 45
Desorber pressure	bar(a)	1.75
Solvent regeneration temperature	°C	120
CO ₂ capture rate	%	90

The CESAR1 solvent was prepared from the individual amine components in aqueous solution (3.0 molar AMP (2-Amino-2-methylpropan-1-ol), and 1.5 molar PZ (piperazine)). The amine component AMP for CESAR1 has been provided by BCH Brühl - Chemikalien Handel GmbH as 90% solution. PZ was provided as anhydrous chips by Julius Hoesch GmbH. The piperazine chips were dissolved in pre-heated water and a solution with 30% PZ was prepared. The final composition of CESAR1 according to the target concentrations of AMP (26.7 wt%) and PZ (12.9 wt%) was produced by mixing the two solutions in the tank of the capture plant. No additives or corrosion inhibitors have been used. The concentration of AMP and PZ and the concentration ratio AMP/PZ were not kept constant in the solvent, but the water content. With increasing content of degradation products and trace components in the solvent the amine concentrations decreased, and the solvent circulation was moderately increased (from approx. 2,600 kg/h to 3,100 kg/h within 21,600 h) in order to keep the CO₂ capture rate of 90%. After removing the major part of contaminants by ion exchange the solvent circulation could be reduced to the initial level.

A commercially available silicon-based anti-foaming agent (SAG 7133, BASF; injected amount about 50 ml) was added on rare occasions (one time per month) to the solvent as needed, when fluctuations of the differential pressure in the desorber column indicated incipient foaming. After using the second tested active carbon quality the need for dosing drastically increased (every one to two days)).

To compensate the solvent losses by sampling, degradation and emissions and to remain the operability of the capture plant regarding the necessary solvent inventory fresh solvent was refilled nine times (between 10 and 30% of the solvent inventory of the capture plant per refill): refills after 79 days (1,896 h), 280 days (6,720 h), 315 days (7,560 h), 458 days (10,992 h), 637 days (15,288 h), 784 days (18,816 h), 970 days (23,280 h), 1,078 days (25,872 h) and 1,241 days (29,784 h) from the solvent tank (3 molar AMP, 1,5 molar PZ, aqueous solution; in refill eight the initial amine ratio was adjusted). This means the volume equivalent to one solvent inventory was added to the plant in a period between 600 and 800 days. For comparison, as

a result of the ALIGN-CCUS long-term campaign with MEA, the solvent inventory change rate was estimated between 200 and 270 days.

Solvent management comprises also a careful control of amine emissions. After parameter studies using CESAR1 and testing of the dynamic behaviour of the different emission mitigation systems of the capture plant at Niederaussem (water wash, acid wash, dry bed, flue gas pre-treatment, wet electrostatic precipitator) the dry bed configuration was almost continuously used from day 400 (9,600 h) in addition to the normal water wash at the head of the CO₂ absorber column to effectively minimise the AMP and PZ emissions. This significantly reduces the emissions without generating waste streams (reduction of AMP from 35 mg/m³ to < 5 mg/m³ and PZ from 10 mg/m³ to <3 mg/m³).

After 400 days (9,600 hours) of testing, the specific solvent consumption was approx. 0.45 kg/tCO₂ for CESAR1. This value takes into account the amine concentration of the solvent, the solvent filling levels in different components of the capture plant, the amount of solvent removed from the process for analysis by sampling (approx. 0.05 kg/tCO₂) and the batch-wise addition of CESAR1 into the process (refills).

The testing campaign with CESAR1 started on 08.04.2019 and the capture plant was almost continuously operated. During the usually short times when no CO₂ was available from the power plant unit it was operated in "hot mode". During the "hot mode" the solvent cycle is maintained and the solvent temperature in the desorber is kept at approx. 85°-100°C, but the flue gas feed is stopped and no CO₂ is captured. This mode of operation was chosen to further thermally stress the solvent allowing continued solvent degradation and release of metal ions into the solvent by corrosion. During the phase of a major overhaul of the power plant from the end of July to the beginning of October 2020, and during a short stop in December 2020 the solvent was drained into the solvent tank, which was emptied from fresh solvent before.

Additionally, three tests were carried out to investigate the degradation rate of CESAR1 at elevated desorber pressure of 2.4 bar(a) and corresponding reboiler temperature of 130°C (for 7 days after 337 day testing time, for further 5 days after 354 days, and 7 days after 822 days).

Removal of NO₂ from the flue gas by thiosulfate or thiosulfate/sulfite addition to the circulating aqueous fluid flow of a pre-scrubber of the capture pilot plant was realized in two setups; a spray scrubber (start at 21.04.2020, duration 200 hours) with and without turbulent mixing regime of the flue gas and a column with structured packing (start at 09.08.2021, duration 2000 hours, see deliverable D 5.2.1).

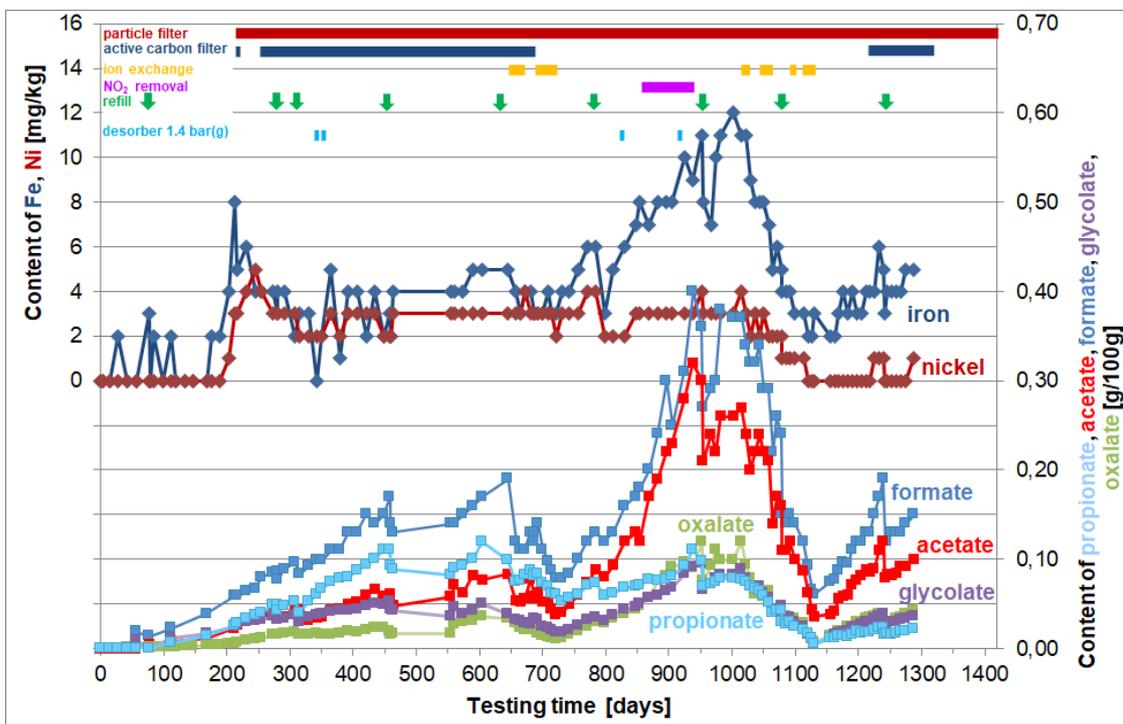


Fig. 2.1: CESAR1 testing campaign at Niederaussem. Till now, the ongoing capture plant was operated 31,000 hours from 09.04.2019. Applied solvent management technologies: refills by adding fresh solvent (green arrows), phases with

elevated desorber pressure (blue bars, 1.4 bar(g) instead of 0.75 bar(g) applied), and phases with active particle filter (dark red bar), active carbon filter (dark blue bars), solvent treatment using ion exchange (yellow bars), and NO₂ removal (magenta bar) by thiosulfate dosing. Additionally, the concentrations of metals (iron, nickel) and of organic acid residues are shown.

1.1. Test of solvent management technologies

The performance of three solvent management technologies (active carbon, NO₂ removal, ion exchange) and their impact on solvent degradation have been evaluated during the still ongoing testing campaign. Additionally, the effect of solvent refills, elevated desorber pressure and temperature, and plant downtime on the degradation rate have been assessed. Figure 2 shows the process configuration and integration points of the solvent management technologies in the process of the CO₂ post-combustion capture pilot plant at Niederaussem which are discussed in this deliverable.

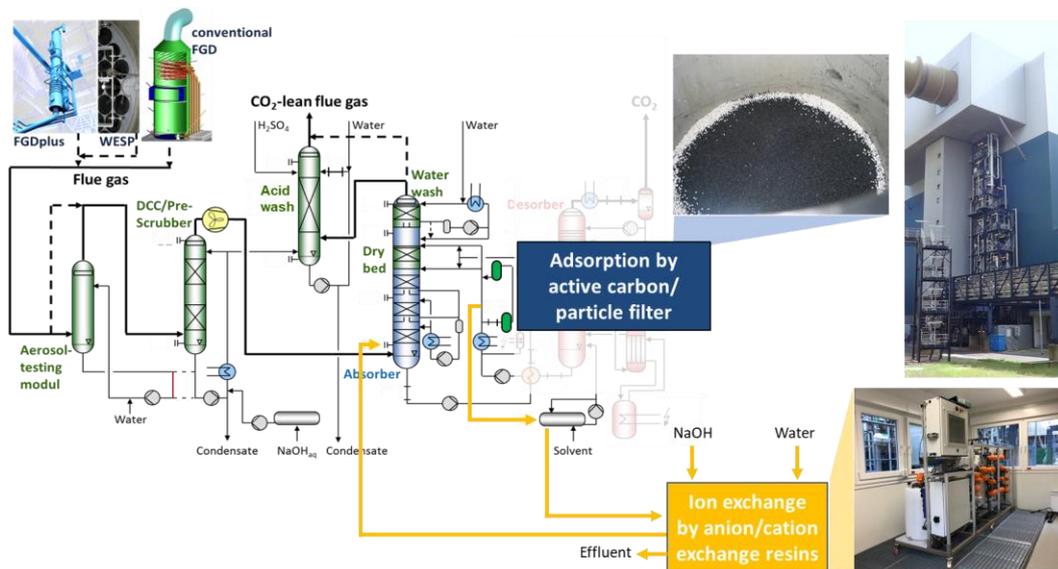


Fig. 2. Integration points of the solvent management technologies in the process of the CO₂ post-combustion capture pilot plant at Niederaussem: Active carbon and particle filter in the lean solvent line and feeding of the solvent treated by ion exchange with cation and anion exchange resins into the absorber.

Table 2 shows the total testing times of the individual technologies and the coloured bars chart in Figure 1 mark the periods of application.

Table 2. Testing periods for the individual solvent management technologies (total testing time 31,000 h).

Parameter	Unit	Value
Total testing time with operation of the active carbon filter	h	12,340
Total testing time active carbon quality A	h	10,452
Total testing time active carbon quality B (until now)	h	1,888
Total testing time with ion exchange using solely an anion exchange resin	h	1,392
Total testing time with ion exchange using cation and anion ion exchange resins	h	1,536
Total testing time with NO ₂ removal by flue gas pre-treatment with thiosulfate/sulfite	h	1,192
Total testing time with elevated desorber pressure of 1.4 bar(g) instead of 0,75 bar(g)	h	720

2.1.1 Active carbon filter

10% of the total solvent flow can be treated by active carbon in the bypass of the lean-solvent line of the capture pilot plant at Niederaussem (in serial configuration also a particle filter can be operated: Pall, Ultipleat polypropylene filter cartridge, removal rating 10 µm). At a typical solvent inventory in the capture plant of 3,000 kg the active carbon inventory in the filter is approx. 210 kg. The adsorptive removal of solvent contaminants by active carbon was investigated in two campaigns using two different qualities of commercially available active carbons.

Active carbon quality A: Granular material with a particle diameter of 0.6-2,36 mm (Type L 8x30 C from Wocklum Chemie; steam-activated active carbon produced from coconuts by pyrolysis; with a specific BET surface of 1,100 m²/g and a density of 1,050 g/cm³). After 216 days of operation (5,184 h), the active carbon filter was activated for the first time, but only for 12 hours. In parallel, the particle filter was activated and continuously operated after then. After day 252 (6,048 h) of the testing program, the active carbon filter was also continuously operated until day 687 (16,488 h).

Active carbon quality B: Granular material from NORIT (type CAC 830W), particle size > 2.36 mm maximal 15%, < 0.60 mm maximal 5%, moisture content as packed maximal 5%, total surface area (BET) 1,100 m²/g, density (backwashed and drained) 445 kg/m³, ball-pan hardness 97, effective size 0.9 mm, ash content 12 wt.-%, content of water soluble ash 0.1 wt.-%. The filter with the second active carbon quality was used from day 1,213 (29,112 h) until today.

2.1.2 Ion exchange with anion exchange resin and serial configuration of cation and anion exchange resins

To evaluate the effects of solvent treatment by ion exchange a mobile system (MIONTEC) was used. Proprietary anion and cation exchange resins provided by the supplier of the ion exchange system were used to remove ionic trace elements from the solvent. In the first campaign the solvent treatment system was first activated after 646 days (15,504 h) of operation. During each ion exchange cycle, approx. 130 l of solvent were treated, corresponding to ca. 4% of the inventory. After each cycle, the resin was regenerated with 4 wt.% NaOH solution. After 17 ion exchange cycles (approx. 2.2 m³ of solvent treated, or approx. 75% of the total solvent inventory), the solvent treatment was stopped for 18 days to monitor the behavior of the solvent degradation and the concentrations of the trace components in the solvent. After 687 days (16,488 h), the ion exchange module was operated again until in total 48 ion exchange cycles have been carried out on day 721 (17,304 h). Approx. 6.2 m³ of solvent were treated in total or approx. 2 times the total inventory.

It is noted that after 690 days (16,560 h) the particle and active carbon filter line was closed and emptied into the solvent loop of the capture plant to refill the plant without adding fresh solvent to the solvent hold up.

The second campaign was conducted with a serial configuration of two separate columns with cation exchange resin in the first step and an anion exchange resin in the second treatment step. In total 92 ion exchange cycles were realized from day 1,016 (24,384 h) until day 1,131 (27,120 h). The campaign was divided into four periods (sequence: 16 cycles (day 1,016 – 1,030), 24 cycles (day 1,044 – 1,064), 11 cycles (day 1,092 – 1,101), and 41 cycles (day 1,110 – 1,130)). In the second campaign, approx. 4 times the solvent inventory was treated. While the anionic exchange resin was regenerated in the same way as in the first campaign, the cation exchange resin needed no regeneration because of the low metal cation concentration in the solvent.

2.1.3 Analysis of solvent and gas streams

Beside the investigation of the concentrations of trace components and organic acids in the solvent by an independent, certified measurement institute (SGS Chemie-, Industrie- und Spezialanalytik; elements (iron, nickel, sulfur) analysed by ICP-OES; anions of carbonic acids (acetate, free glycolate, formate, oxalate and propionate) and inorganic anions (chlorine, nitrate, sulfate) by ion chromatography (limit of quantification: sulfur <20 mg/kg, iron <1 mg/kg, nickel <1 mg/kg, and other anions <2 mg/kg)) also the concentrations of some amine reaction products were analysed by an independent, certified-measurement institute (HENKEL; ethane-1,2-diamine (EDA), 1-formylpiperazine (FPZ), 2-oxopiperazin (OPZ)), analysed by liquid

chromatography and ESI-MS). Additionally, the solvent samples were analysed directly at Niederaussem in terms of water and amine content, CO₂-loading and, qualitatively (uncalibrated), regarding degradation products (Karl-Fischer titration Eco KF Titrator and CO₂ titration Eco Titrator Oil from Metrohm, and Gas Chromatograph (GC) system Agilent 7890B). Also the concentrations of uncalibrated compounds in the chromatogram are semi-quantitatively detected based on the area of the respective signals and an internal standard of the GC. By titration of CO₂-free solvent samples with KOH solution (Titrande from Metrohm; TitriPUR 0.1 mol/l KOH in ethanol) the acid number was determined which represents the total concentration of acids (inorganic and organic) and is quoted as formic acid equivalents (consumption of 1 mol KOH at the equivalence point corresponds to 1 mol (46.03 g) formic acid equivalents).

Acid number and the concentration of uncalibrated compounds are integral values for the degradation products in the solvent and allow to evaluate the level of degradation, even if not all degradation products are known. Figure 3 shows that the acid number and the content of uncalibrated compounds are highly correlated which indicates that both semi-quantitative values represent the level of solvent contamination well and that no important “hidden compounds” exist which are dominating the degradation processes in the unknown background of the solvent matrix. As expected, at lowest acid numbers (which means at the beginning of the campaign with fresh CESAR1) the content of uncalibrated compounds is lower than for the aged solvent. In addition, ion exchange removes slightly more acids from the solvent than uncalibrated compounds.

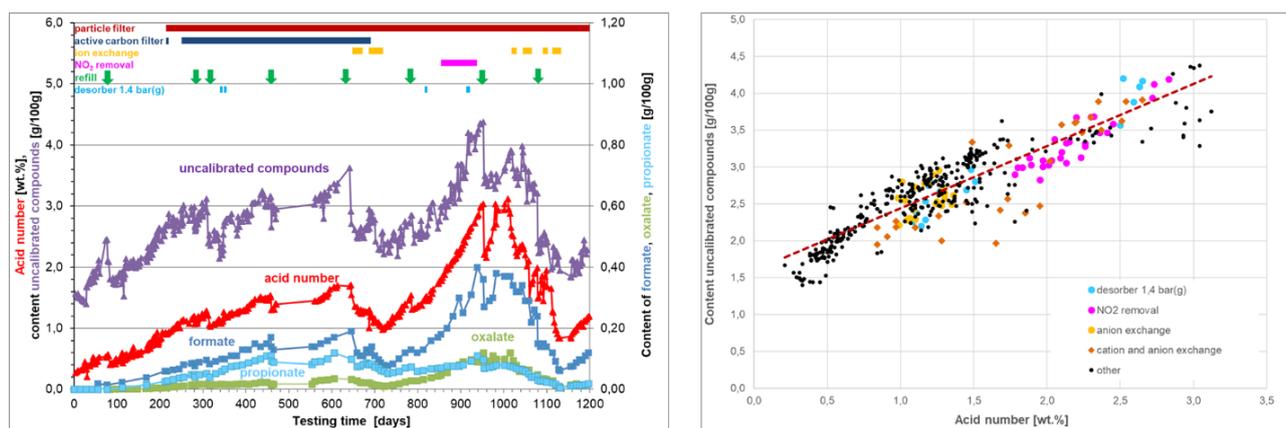


Fig. 3. Acid number and content of uncalibrated compounds are semi-quantitative and integral measures for the level of contamination of the solvent (left diagram). They comprise also unknown species in the solvent. Both are highly correlated (right diagram). Taking into consideration the effects of solvent management technologies on both measures the scattering is relative low.

3 Results

3.1 Effect of solvent treatment with active carbon

Solvent treatment by active carbon is usually applied in capture plants to avoid operational issues - like foaming - although the exact effect mechanism is not completely clear. Active carbon effectively adsorbs specific contaminants because of its large surface area, large number of surface-active adsorption sites (also functional groups like O–H and/or N–H groups are available as well as metal oxides and hydroxides), and high adsorption capacity. The interaction of the metal ions and complexes with the active carbon (more exactly with the reactive binding chemical groups at the graphitic-like surface as -COO⁻ or hetero atoms as N and S) can be interpreted as a special case of ion exchange.

As the proposed guiding principle “amine-based solvents should generally be clear and transparent” links the colour and transparency of the solvent with the degradation rate, application of active carbon leading to colour removal should reduce the amine degradation rate and the accumulation of the degradation products in the solvent [1]. However, for the hypothesis that colouring contaminants are accelerating the degradation and lowering the performance of the solvent, no evidence is resulting from the long-time test of CESAR1 at all.

3.1.1 Active carbon A

When the active carbon A was applied, it removed colouring contaminants from the solvent, see Figure 4. Additionally, the concentrations of iron and nickel are reduced (iron from 8 to 4 mg/kg and below the detection limit after to refills; nickel from 5 to 3 mg/kg and after the refills down to 2 mg/kg). Also the accumulation of chloride in the solvent is stopped which is exactly what is proposed for these three specific contaminants named in [1] to ensure satisfactory capture plant operation, see Figure 5.

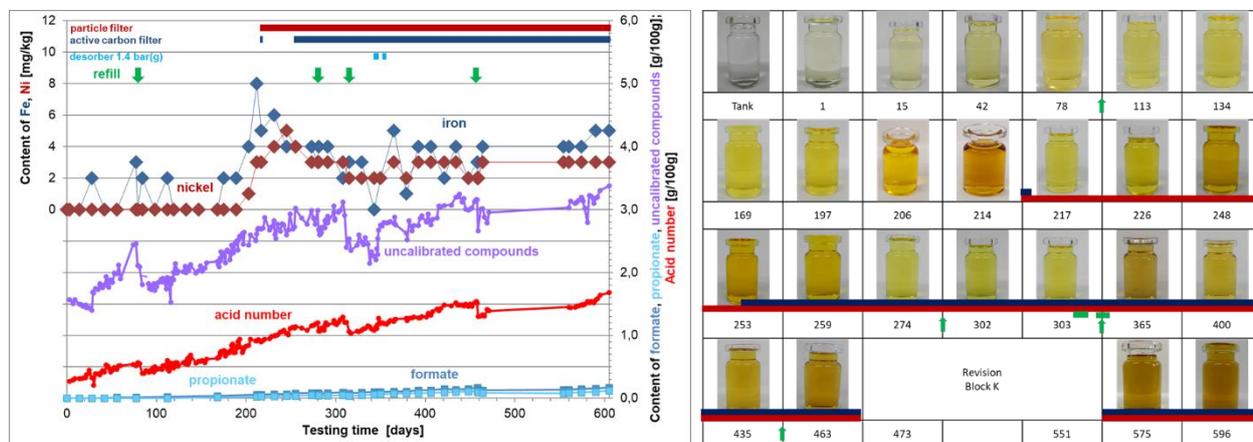


Fig. 4. Active carbon A is able to remove a part of the solved iron and nickel from the solvent (left diagram). Although the colouring components are not known, it is obvious that application of active carbon is reducing the visible absorbance of the solvent and removes some colouring agents from the solvent (right photos from solvent samples). The period of operation of the active carbon filter is marked in both diagrams by the dark blue bar.

In contradiction to the proposed guiding principle, there is no effect of active carbon on the increase of the concentration of degradation products (the increase represents the difference between formation and decomposition of the respective degradation product). The results indicate that the colour and transparency of the solvent is meaningless for evaluating the solvent performance and the solvent degradation rate. For more than 600 days (and before the concentrations are changed by application of ion exchange), the accumulation of amine degradation products in the solvent follows a linear trend. Figure 4 shows especially that there is no correlation between the acid number (indicator for degradation) and the metal content in the solvent, indicating that the role of metal ions in the solvent degradation must be reassessed.

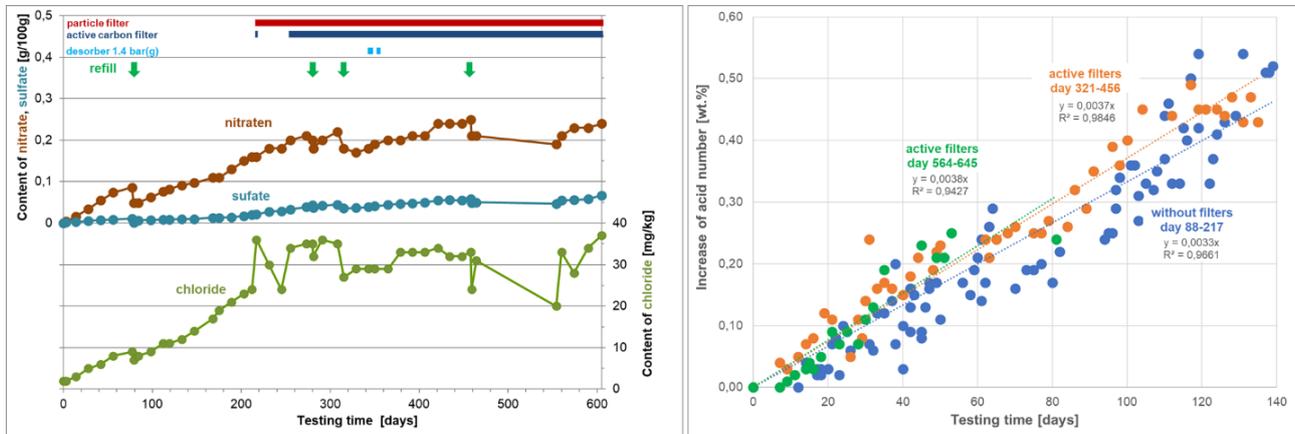


Fig. 5. Active carbon A is able to remove a part of chloride from the solvent, but no nitrate and sulphate anions (left diagram). There is no effect of the active carbon filter on the rate of accumulation of acidic degradation products in the solvent – expressed by the increases of the acid number – (right diagram) before and after the activation of the filter.

3.1.2 Active carbon B

When the active carbon B was applied, again a reduction of the visible absorbance of the aged CESAR1 solvent could be observed, see Figure 6.

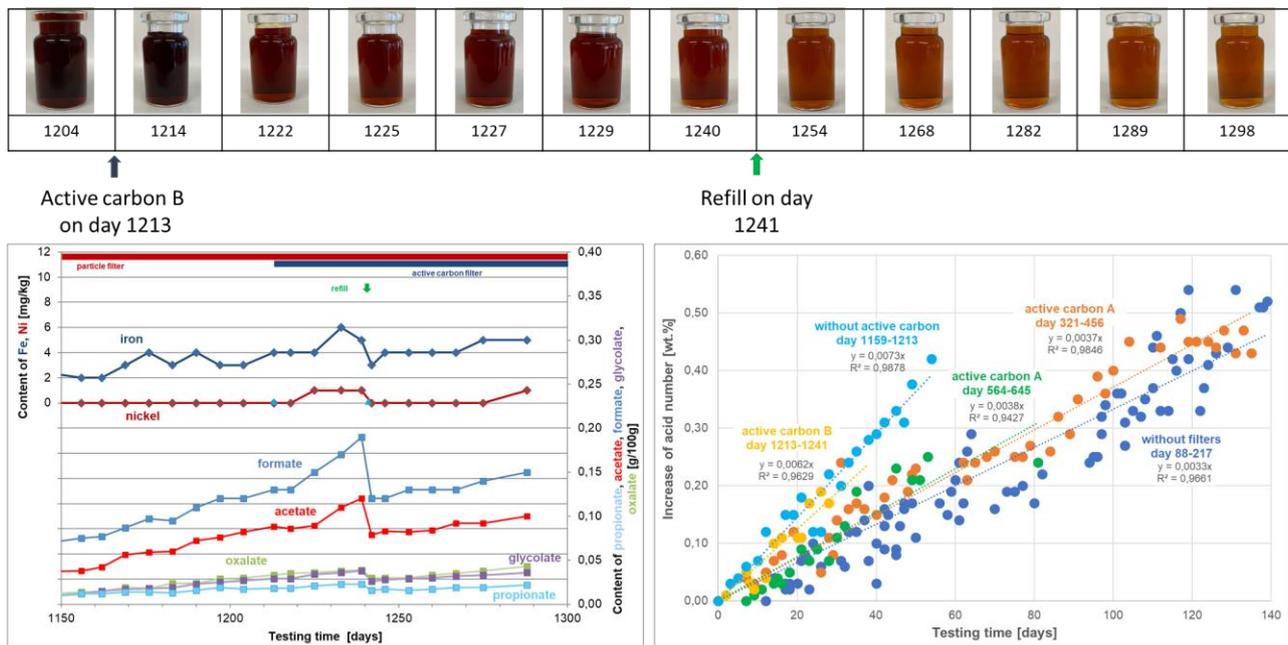


Fig. 6. Active carbon B was – in contrast to active carbon A – not able to remove iron, nickel or chloride from the solvent or organic acid residues (left diagram). There is no significant effect of the active carbon filter on the rate of accumulation of acidic degradation products in the solvent – expressed by the increases of the acid number – (right diagram) before and after the activation of the filter with active carbon B.

But in contrast to active carbon A no organic or inorganic trace components could be removed from the solvent. Additionally, no significant change of the increase rates of the semiquantitative, integral measures for the solvent degradation – acid number and uncalibrated compounds found in the GC-analysis of the solvent – could be detected. Also no correlation between the analysis data and the strong increase in the

demand on anti-foaming agent which directly started after the start of the adsorptive removal of contaminants from the solvent with active carbon B could be identified.

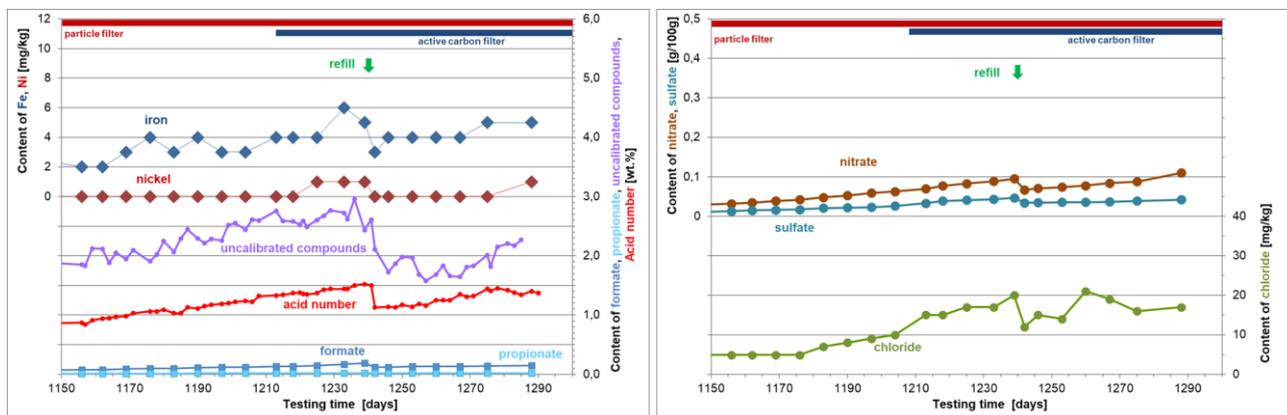


Fig. 7. Application of active carbon B did not result in a reduction of any contaminant that is analysed quantitative (metals, organic acid residues) and semi-quantitative, integral measures (acid number and uncalibrated components from the GC analysis; left diagram) and inorganic anions (right diagram).

3.2 Effect of ion exchange

To prepare the testing campaign at the pilot plant at Niederaussem first laboratory tests with an anionic and three different cation exchange resins were carried. Table 3 shows results for an anion exchange resin and three cation exchange resins. One objective of special interest was to evaluate the potential of the removal of specific metal ions from the aged CESAR1 solvent (sample after 645 days of solvent testing; before the start of the reclaiming). The results show that the Type “Anionic resin” manages to remove iron, chrome and zinc from the solvent which clearly confirms the presence of anionic complexes of these metal ions in the solvent and therefore the importance to consider the entirety of the components in the solvent for the explanation of degradation mechanisms and rates. This implies also that complex formation must be regarded more detailed in laboratory degradation tests to receive meaningful results and to avoid oversimplification of the experimental set-up.

Table 3. Analysis results for the removal of four metals from CESAR1 by four different resins (and reduction rates).

Resin	Fe [mg/l]	Ni [mg/l]	Zn [mg/l]	Cr [mg/l]
Untreated CESAR1 benchmark	5.2	3.4	1.4	1.5
Anionic resin	0.33 (94%)	3.8 (0%)	0.260 (81%)	0.79 (47%)
Type A (cationic resin)	1.7 (67%)	1.5 (56%)	0.003 (100%)	1.5 (0%)
Type B (cationic resin)	1.5 (71%)	3.3 (3%)	0.003 (100%)	1.4 (7%)
Type C (cationic resin)	5.1 (2%)	2.6 (24%)	0.440 (69%)	1.5 (0%)

The cationic resins Type A and B both allow removing a large share of iron and zinc ions from the solvent, but show different removal capabilities for nickel. It was from high interest to use the campaign at the capture pilot plant at Niederaussem to investigate how the specific removal of e.g. iron influences the solvent degradation rate and the degradation mechanisms. The cationic resin Type C showed a lower removal performance for all three metals.

Table 4 shows the result of a consecutive application of an cationic exchange resin (cationic resin Type A, solvent sample from day 687; 16,488 h) for the effluent of the exchange column after a reclaiming cycle

with the anionic exchange resin. Except for chrome all metal concentrations could be further reduced by the cationic exchange resin, especially zinc, manganese and vanadium.

For the campaign in the capture plant with serial application of cationic and anionic exchange the cationic resin A was selected.

Table 4. Metal removal from CESAR1 by consecutive application of anionic and cationic ion exchange resins.

Resin	Fe [mg/l]	Ni [mg/l]	Cr [mg/l]	Zn [mg/l]	Mn [mg/l]	V [mg/l]
Anionic resin	2.9	2.4	1.0	1.1	0.47	0.0010
Type A	1.6	1.7	1.1	0.0052	0.0092	<0.001

3.2.1 Anion exchange

The results of the removal of anions from the solvent by an anion exchange resin are contrary to the operational philosophy “keep the solvent clean”. The concentration of anions could be significantly reduced by more than 50% after treating the solvent inventory in total 2 times, see Figure 8 and Table 5. The anionic ion exchange resin can remove a significant portion of the iron content from the solvent, but less or no nickel. Also the concentration of zinc and chromium can be significantly reduced [3]. This result implies that metal cations which are dissolved in the solvent partially exist as anionic complexes and underpins also the importance of the solvent matrix for the properties and the catalytic effects of metal ions on amine degradation, as the properties of the ligands can control the redox behavior and the catalytic activity of a complexed metal ion.

However, decisive for the solvent management is how the solvent degradation rate is influenced by the removal of metals and degradation products and trace components which might act as ligands and can tune the redox behavior of metals and the degradation mechanisms. Directly after the completion of the anion exchange campaign, the rate of increase of the acid number doubled and the rate of increase for uncalibrated compounds even rose by a factor of 4.6. While the increase of the acid number remained high, in the following 100 days of operation, the accumulation of uncalibrated compounds slowed down, but remained higher than before the anion exchange, see Figure 9.

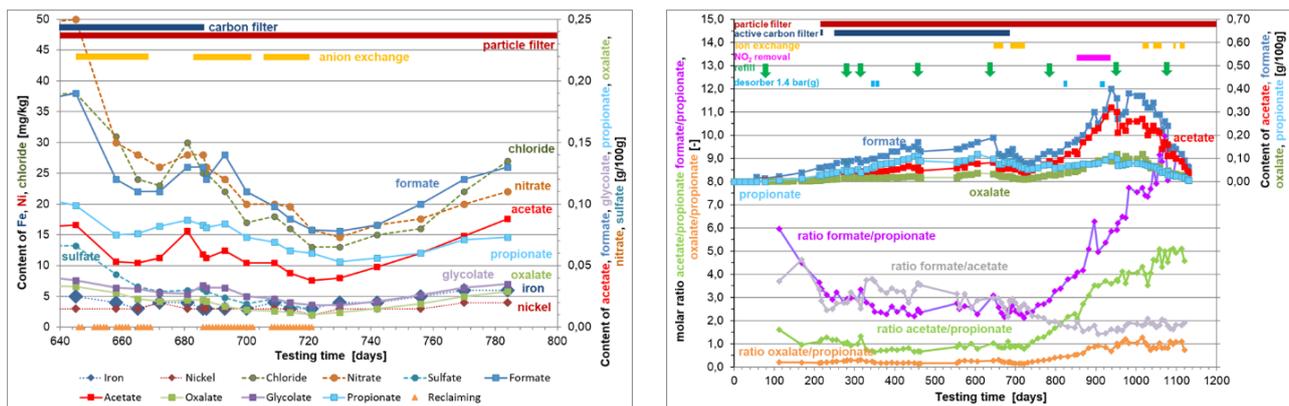


Fig. 8. Left diagram: Removal of trace components and oxidative degradation products from the CESAR1 solvent by ion exchange using an anion exchange resin and fast increase of their concentrations after the solvent treatment. In total 48 cycles were applied (start day 645 (15,480 h), end 721 (17,304 h)). Before the start of the last 31 ion exchange cycles, the active carbon filter was deactivated. Right diagram: Reducing the content of anionic contaminants like formate, acetate, oxalate and propionate caused a steep increase of the solvent degradation. The change of the molar ratio of organic acid residues related to the content of propionate indicates a prompt change of the degradation behaviour of the solvent.

Table 5. Reduction of the concentrations of contaminants in the CESAR1 solvent by the application of anion exchange.

Concentrations	Fe [mg/kg]	Ni [mg/kg]	chloride [mg/kg]	nitrate [wt.%]	sulfate [wt.%]	formate [wt.%]	acetate [wt.%]	glycolate [wt.%]	oxalate [wt.%]	propionate [wt.%]
Before anion exchange	5	3	38	0.25	0.066	0.19	0.083	0.038	0.033	0.099
After anion exchange	3	2	13	0.079	0.014	0.079	0.038	0.018	0.01	0.06
Reduction [%]	40	33	66	68	79	58	54	53	70	39

Figure 8 shows that the accumulation of propionate in the degrading solvent differs from that of acetate and formate. A clear change in the degradation behaviour of CESAR1 can be identified due to the removal of anions from the solvent. It remains unclear if the formation of propionate was slowed down or if the degradation product propionate itself is faster degraded. It is postulated that propionate forms from condensation of the two partly oxidised degradation products formaldehyde and acetaldehyde via acrolein that is reduced by ammonium acetate [4]. As formaldehyde is a primary target for oxidizing species it is likely that its concentration is strongly decreased by a more aggressive oxidative environment after the anion removal, so that less propionate is formed. In any case, this is an indication that cleaning the solvent by removing anionic compounds not only changed the total rate of solvent degradation, but also the relative rate of different degradation pathways.

The purpose of the proposed operational philosophy “keep the solvent clean” would be to keep solvent degradation controlled at a low rate. The steep increase of the level of degradation observed directly after the anion exchange campaigns, shown in Figure 9, is the exact opposite effect. The increased degradation rate occurred although the concentration of anionic compounds and iron have been reduced to levels which are lower than 12,000 operating hours before. However, this failure of the concept to remove contaminants preventively from the solvent to reduce solvent losses, together with the confirmation that metal ions which are potentially catalyzing degradation reactions exist as negative charged complexes in the solvent, opens the way to better understand and control the degradation mechanisms in amine-based solvents.

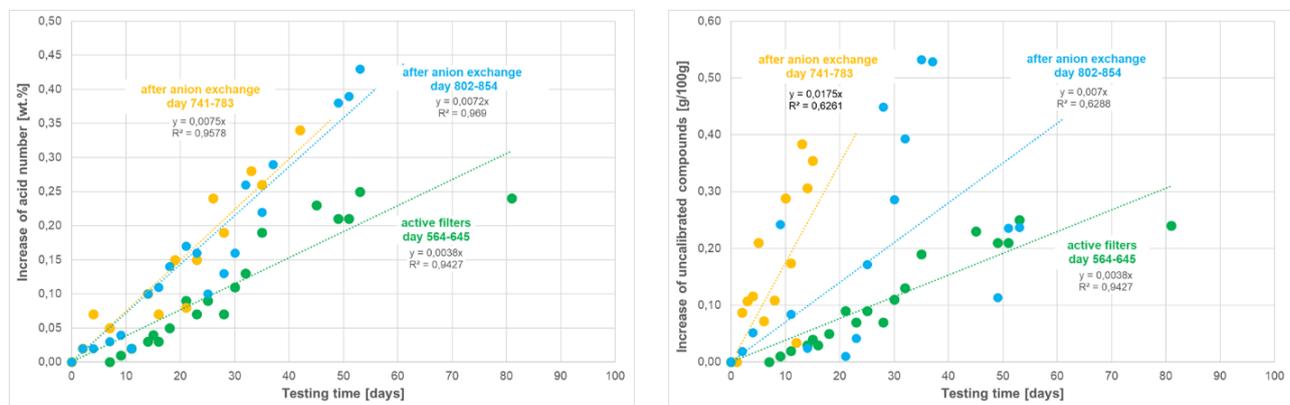


Fig. 9. Although significant amounts of complexed metal ions and anionic inorganic and organic anions have been removed by the anion exchange resin the increase of the acid number (left diagram) and the uncalibrated compounds (right diagram) was much faster than before the anion exchange started (green line: “active filters” is the period before the anion exchange).

In connection with the determination of the frequency of applying anion exchange which is necessary to keep the concentration of anions constant in the solvent, the concentrations of contaminants in the solvent before and after anion exchange was investigated. Table 6 shows the effect of the first reclaiming cycle (number 18 from in total 48 cycles) after a period of 18 days without reclaiming (day 687; 16,488 h) to compare the concentrations of the solvent from the capture plant entering the exchange column and of the solvent leaving the ion exchanger. It seems that already all anionic iron complexes have been removed from the solvent in the first 17 cycles as the removal rate is now 0%. To remove the remaining positive charged

iron complexes a cation exchange resin is needed, which was tested in the second ion exchange campaign from day 1,016 until day 1,131 of the testing campaign.

Amine losses, in both the sweetening and the regeneration steps of the ion exchange cycle as well as the generated amine-loaded waste streams, occur in every cycle and can be reduced by modifying the operating parameters and integration configuration of the ion exchange plant into the capture plant process (to avoid dilution of the solvent with rinsing water). A detailed analysis of the effort to keep the concentrations of contaminants constant by ion exchange was carried out for the serial configuration of cationic and anionic exchange resins based on the test results.

Table 6: Concentration of trace components and oxidative degradation products in the solvent entering and leaving the anion exchange resin and calculated removal.

	Parameter	upstream reclaiming	downstream reclaiming	Removal (%)
Metals	Iron [mg/kg]	3	3	0
	Nickel [mg/kg]	3	3	0
Impurities	Sulfur [mg/kg]	90	<10	> 88%
	Sulfate [mg/kg]	290	15	95%
	Chloride [mg/kg]	25	7	72%
	Nitrate [mg/kg]	1300	640	51%
Degradation products	Formate [mg/kg]	1200	180	85%
	Acetate [mg/kg]	560	<50	> 91%
	Oxalate [mg/kg]	99	13	87%
	Glycolate [mg/kg]	320	<50	> 84%
	Propionate [mg/kg]	810	340	58%
	Ammonium [mg/l]	33000	34000	ND

3.2.2 Cation and anion exchange

The removal of contaminants by applying a cation and an anion exchange resin in serial configuration reduced the concentrations of impurities and metals to levels which have been determined after 130 and 210 days of operation at the beginning of the overall CESAR1 testing campaign and before the first time particle and active carbon filters have been activated, see Figure 10. The achieved reductions are between 73 (iron) and 100% (nickel), see Table 7. The concentrations of the organic acid residues could be reduced by >80%. The removal of contaminants by serial application of cation and anion exchange resins resulted in a reduction of the solvent degradation, see Figure 11. The increase rate of the acid number has been reduced to 1/3 of the rate before cation and anion ion exchange (and after the campaign on NO₂ removal from the flue gas, which resulted in the highest increase rate of the accumulation of degradation products in the solvent of the overall CESAR1 campaign).

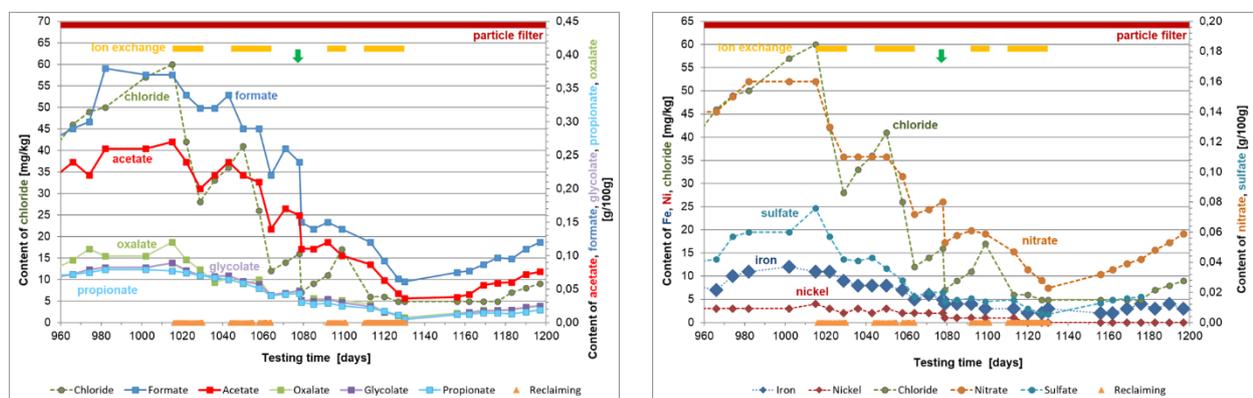


Fig.10: Removal of oxidative degradation products (left diagram) and metal ions and inorganic anions (right diagram) from the CESAR1 solvent by 92 ion exchange cycles (orange triangles) using a serial configuration of cation and anion exchange resins. The

concentrations of metal ions, inorganic anions and organic acid residues have been reduced to levels below the concentrations determined in the period <210 days of operation at the beginning of the overall campaign.

Table 7. Removal of contaminants in the CESAR1 solvent by the application of anion and cation exchange.

Concentrations	Fe [mg/kg]	Ni [mg/kg]	chloride [mg/kg]	nitrate [wt.%]	sulfate [wt.%]	formate [wt.%]	acetate [wt.%]	glycolate [wt.%]	oxalate [wt.%]	propionate [wt.%]
Before cation/anion exchange	11	4	60	0.16	0.076	0.059	0.27	0.089	0.12	0.077
After cation/anion exchange	3	0	<5	0.023	0.0054	0.079	0.036	0.005	0.0076	0.005
Reduction [%]	73	100	92	86	93	84	87	94	94	94

It is instructive to compare the rates of accumulation of the acidic components in fresh CESAR1 (from campaign day 0 to 74), in the phase after the first refill and before the particle and active carbon filters were activated for the first time (from campaign day 77 to 216), and in the phases after the application of anion exchange (from campaign day 741 to 783 and after refill at day 784 from 802 to 854), and cation and anion exchange (from day 1,159 to 1,200). After removing anions and cations from the solvent, the degradation rate, expressed by the increase rate of the acid number, is similar to the rate after anion exchange only. The lowest increase rate is not found for the fresh, most clean solvent, but for mildly aged solvent without any application of solvent management. Taking into consideration that before the stepwise increase of the acid number after the anion exchange (day >741), the increase rate of the acid number was lower than at the beginning of the overall campaign (day 0 to 74), it becomes clear, that preventive cleaning of the CESAR1 solvent does not lead to an improvement.

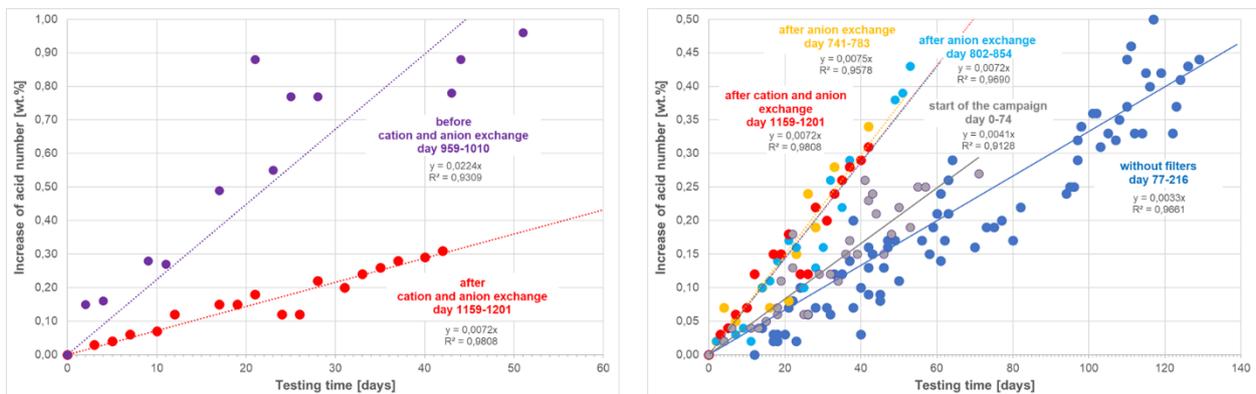


Fig. 12. Application of ion exchange with serial configuration of cation and anion exchange resins significantly reduced the formation and accumulation of acidic degradation compounds in CESAR1 (left diagram), but the achieved increase rate of the acid number shows no difference compared to the rate after anion exchange. The lowest rate of increase is not for fresh solvent, but for an aged solvent

In connection with the work of WP6 on the economics of the different solvent management technologies it was investigated how often the combined cation and anion exchange must be applied to keep the concentrations of contaminants in the solvent constant. The effect of cation and ion exchange allows to remove contaminants (here the acid number was used as measure of the solvent contamination with degradation products, trace components and corrosion products, representing the sum of all acidic compounds in the solvent) faster from the solvent than their formation or addition to the solvent is. Figure 13 shows the resulting “negative” trends for the acid number during the ion exchange campaign with cationic and anionic exchange resins.

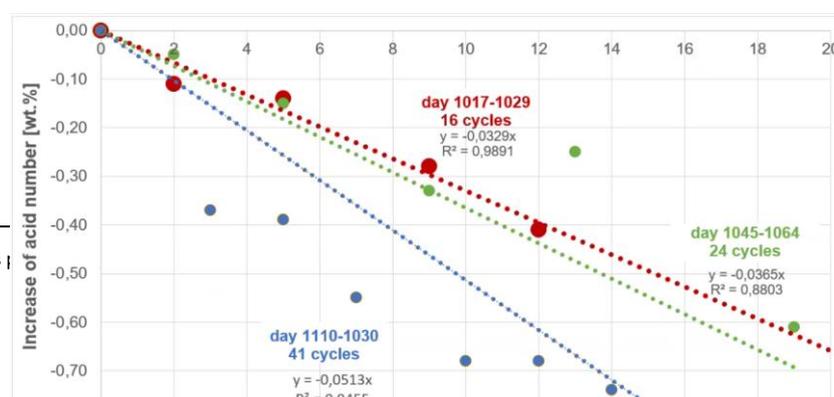


Fig. 13. Decrease of the acid number during ion exchange with anionic and cationic exchange resin.

Combining the results shown in Figure 12 and 13, the increase rate of the acid number is 0,0072 wt.-%/d due to degradation, while the decrease during ion exchange is -0,0329 wt.-%/d. Here the removal rate is the sum of increase and decrease and depends on the frequency of ion exchange cycles, e.g. 16 cycles in 12 days (Removal per cycle: $-(0,0329+0,0072)$ wt.-%/d / (16 cycles/12 d)= -0,03 wt.-%/cycle).

The theoretical frequency of ion exchange cycles to keep the acid number constant is $0,03/0,0072$ d/cycle = 4,2 d/cycle. For the other two phases shown in Figure 13 the result is 4,8 and 4,0 d/cycle which means an average of 4,3 d/cycle

About 70 g of amine per ion exchange cycle have been lost which is only 0.0058% of the amine inventory. Additionally, 90 kg/cycle of 4 wt.-% NaOH solution are consumed and 245 kg/cycle wastewater are generated (composition shown in Table 8).

Table 8. Concentrations of contaminants in the waste water from the anion and cation exchange.

Concentrations	Fe	Ni	chloride	nitrate	sulfate	formate	acetate	glycolate	oxalate	propionate
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
	0	0	10	350	146	541	271	143	46	249

4 Solvent matrix, complex formation and catalytic activity of metals

4.1 The role of ligands on catalytic effect of metal ions

After 25,000 testing hours at the capture pilot plant at Niederaussem, the concentration of iron in the CESAR1 solvent reached concentrations around 10 mg/l (0.19 mmol/l). Assuming that all iron atoms are present as dissolved Fe^{3+} ions which oxidatively attack AMP and PZ according to their molar ratio, the calculation of the specific amine loss results in only 0.016 g/l (0.011 g/l AMP and 0.005 g/l PZ). As the amine concentration is 400 g/l, it becomes immediately clear that an oxidation mechanism based on iron is negligible in the case that Fe(III) is only consumed (and transformed to Fe(II)) and not somehow recovered.

The oxidative degradation of amines is commonly explained by the formation of amine radicals initiated by the reaction with dissolved oxygen molecules under the formation of hydroperoxides [5,6]. The direct reaction between oxygen and an organic molecule has a high activation energy. Based on laboratory experiments, it is often supposed that dissolved transition metal ions can catalyze the amine oxidation process as reactive radicals are formed when the metal ion (especially Fe^{3+}) takes up an electron. However, it must be taken into account that the dissolved cations in the solvent are not "free", but are complexed by anions or non-ionic amines and water or degradation products. The redox property of a metal in a complex differs significantly from its free state. In complexed form, the ability of a metal ion to get oxidised or reduced is determined by the overall tendency of the complex for this redox-process. The coordination is strongly dependent on the solvent matrix, salt concentration and the pH value (which could explain differences in the solvent stability and consumption at different capture plants fed with different flue gas qualities). For example, in ammonia no iron amine complex is formed, but Fe(III)hydroxide. Especially, chelate-forming polydentate ligands which contain nitrogen and/or oxygen are able to build complexes which are quite stable against oxidation of the ligands, as the well-known yellow $[\text{Fe}(\text{EDTA})(\text{H}_2\text{O})]^-$ (EDTA:

ethylenediaminetetraacetic acid), $[\text{Fe}(\text{en})_2\text{Cl}_2]^+$ (en: ethylene diamine), and the green complex $[\text{Fe}(\text{ox})_3]^{3-}$ (ox: oxalate). Also complexes with positive charges are known as the red brown $[\text{Fe}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]^+$ (OAc: acetate), and zinc and chromium form a plethora of complexes with species that are available as ligands in the degraded CESAR1 solvent (e.g. $[\text{Zn}(\text{OAc})_4]^{2-}$, $[\text{Zn}(\text{en})_3]^{2+}$, $[\text{Cr}(\text{ox})_3]^{3-}$, $[\text{Cr}(\text{en})_3]^{3+}$, $[\text{Cr}_3\text{O}(\text{OAc})_6(\text{OH})_2]^+$). Figure 14 shows exemplary some complexes of iron.

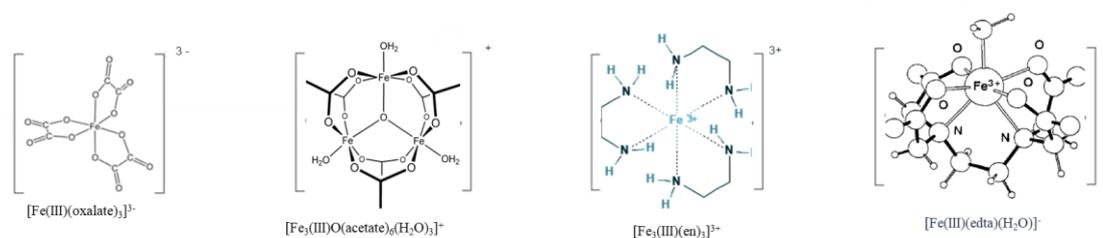


Fig. 14. Some positive and negative charged complexes of iron.

The ligand-controlled chemical activity of transition metals is used for a wide range of technical processes (e.g. N- and O-donor chelated Fe(III)/Fe(II) complexes as catalysts for the oxidation of hydrogen sulfide to sulfur by air [7]; chromium(III) complexed by acetate, formate, oxalate, or glycolate as tanning agent in the leather production [8]; zinc complexes with N-donor ligands as catalysts in the polymerisation of cyclic esters [9]. It is not exactly known how the electron transfer from the oxidised amine to the metal species mechanistically takes place and we cannot answer today if the redox process has the characteristics of an outer sphere electron transfer (the electron transfer occurs between chemical species that remain separate before, during, and after the redox event) or if the electron transfer occurs in an inner shell based on a strong electronic interaction between the oxidant and the reductant reactants via a covalent or complex linkage. However, to fulfil the definition of a catalyst the oxidising metal cation must be recovered by a redox process, most likely by oxygen from the flue gas which is diluted in the solvent. To allow a Fe(III)/Fe(II) chelate systems to be an effective catalyst of the amine degradation several requirements must be fulfilled [7].

Assuming that only homogeneous catalysis is relevant for the solvent degradation process the stability of the iron(III) complex must be high enough that solid $\text{Fe}(\text{OH})_3$ will not precipitate at the relevant pH value of

the solvent (solubility product of Fe(OH)₃ 2.64x10⁻³⁹mol⁴/l⁴ and of Fe(OH) 4.87x10⁻¹⁷mol³/l³; also the stability of the Fe(II) complex must be high enough to avoid precipitation of Fe(II) salts (e.g. FeCO₃ 3.07x10⁻¹¹ mol²/l² from the solvent; and the difference in the stabilities of the Fe(III) (ferric) and Fe(II) (ferrous) complexes must be low enough so that Fe(III) can be reduced by the oxidised amine and that the resulting Fe(II) complex can be regenerated by aeration of the solution at alkaline conditions. As the pH value of the rich CO₂-loaded CESAR1 solvent is 9.5 ([OH]⁻=10^{-4.5}mol/l) the maximum allowed concentration of Fe³⁺ in the solvent could be 2.64x10⁻³⁹/10^{-13.5} mol/l=8.35x10⁻²⁶ mol/l before Fe(OH)₃ precipitates (maximum [Fe]²⁺ for Fe(OH)₂ is 1.54x10⁻³ mol/l). For the more alkaline lean solvent (pH value of the lean CESAR1 solvent is 11.2, [OH]⁻ is 10^{-2.8} mol/l) the respective maximum iron ion concentrations are for Fe³⁺ 6.63x10⁻³¹mol/l and for Fe²⁺ 1.22x10⁻⁸ mol/l. Actually the maximum (total solved) iron concentration in the lean solvent was around 1.4x10⁻⁴ mol/l, which confirms the relevance of complexation of Fe³⁺ and its possible function as a homogenous catalyst for the amine degradation.

Fe(III)L_n chelates are generally more stable than Fe(II)L_n chelates and investigations for a number of ligands have shown (for 100% excess of the ligand L than needed to form the metal complex and at a concentration of 10⁻² M metal chelate) that -log([Fe(III)L_n]/[Fe(II)L_n]) is varying between 5 and 13 for amino carboxylic acids (N-/O-donor ligands) and up to 21 for other ligands [7]. Fe(III) has a relative preference for the harder ligands containing negative oxygen donors compared to the softer ligands containing a mixture of nitrogen and oxygen donors.

If the Fe(III) chelate is too stable relative to the Fe(II) chelate (-log([Fe(III)L_n]/[Fe(II)L_n]) > 16), the thermodynamic capability of iron to act as a catalyst is low and the chelate prefers to remain in the Fe(III) state. On the other hand if the Fe(II) chelate is too stable the iron cannot be oxidised and act as a catalyst. Figure 15 shows the simplified redox-cycle for the complexed iron when it acts as a catalyst for solvent degradation and oxygen activation.

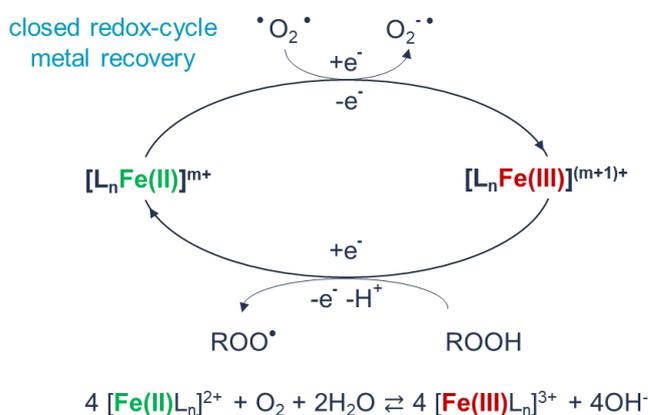


Fig. 15. Simplified scheme of the closed redox-cycle of complexed iron which act as catalyst for solvent degradation and for the activation of oxygen.

The equilibrium constant K for re-oxidation of the ferrous to the ferric chelate by oxygen, which takes place in the solvent with the diluted oxygen from the flue gas (partial pressure of oxygen in the solvent pO₂), is expressed by $K = \frac{[\text{OH}^-](\text{pO}_2)^{1/4}}{[\text{Fe(III)L}_n]/[\text{Fe(II)L}_n]}$. The oxygen solubility in amine-based solvents is typically in the range between 5 and 10 mg/l for CO₂-unloaded solutions. At plant conditions, i.e., CO₂-loaded solutions at 40°C and above, the oxygen content is below 1 mg/l and cannot be properly quantified up to now [10].

Beside degradation products as ethylene diamine, piperazine itself and its derivatives like N-(2-aminoethyl)piperazine can act as ligands [11]. Also some studies on the coordination chemistry of AMP have been published, where AMP ligands showed two types of coordination modes, chelating and bridging [12; 13]. Additionally other ions which are diluted in the solvent (for CESAR1 around 32 g/l of ammonium cations are formed by oxidation of the amine groups) influence the stability constant for the complexation

(salt effect) and the hydration of these ions will affect the water activity and thence initial state, transition state and rate constants of ligand exchanges. These non-electrostatic “outer-sphere” effects will be dominant for reactions involving hydrophobic leaving groups [14] which makes the understanding of the interaction between the metal ion and the solvent amines more complicated, especially when the ligand itself is oxidised. Beside the thermodynamic stability of the complex also the kinetic stability must be considered. Even if a reaction with ligands could lead to a lower free energy of the system (thermodynamic stability) there might be no available mechanism by which the reaction can occur (kinetic stability), although a reaction would lead to a more stable system. However, the slowest part of the re-oxidation of the reduced metal cation might be explained by the dissolution of oxygen from the flue gas to the aqueous phase. Further laboratory experiments can help to identify the importance of these effects on the reactivity of metal ions, for the degradation rate, and the degradation mechanism.

The reactivity of metal ions in chemical and biological systems (e.g. hemoglobin in blood, myoglobin in muscles) comes from the fact that the displacement of ligands is an imported step in complex-formation reactions and in many redox processes. Intensive investigations of the reactivity of Fe(III)/Fe(II) complexes in amine solutions have been carried out in connection with treatment of sour gas streams to remove H₂S by oxidation with O₂ or to reversibly bind NO in gas cleaning applications. Here, especially iron chelate complexes with ligands from the group of aminocarboxylates, like the prominent hexadent ethylenediaminetetraacetate (edta), but also small amino acids have been studied as absorbent [15, 17-19]. Alkanolamines are not used in these industrial processes because of their lower oxidation stability, but this does not mean that they could not form chelate complexes. The chelated iron is oxidation catalyst in aqueous solution and the ligands determine the rate and overall equilibrium constants, as well as the nature of the substitution mechanism by which O₂ or NO coordinate to the selected complexes. The binding in the NO complexes is similar to the coordination of dioxygen to the metal centers, although the nitrosyl products are far more stable. There is, however, no simple correlation between the rate and activation parameters and the selected donor groups or overall charge on the Fe(II) complexes. It was found that high-stability of Fe(III) chelates do not form satisfactory redox catalysts and that ligands that form suitable iron complexes as catalysts have both oxygen and nitrogen donors [17]. However, not only the metal is oxidized, but also the ligands can be attacked [16]. To act as a catalyst in amine degradation, the difference in stabilities of the Fe(III) and Fe(II) chelates must be low enough so that the Fe(III) form can be reduced and that the Fe(III) chelate can be regenerated by the dissolved oxygen in the solvent at alkaline pH. The impact of the ligands becomes clear when exemplarily the redox potential of [Fe(III)(edta)]⁻/[Fe(II)(edta)]²⁻ of 0.129 V is compared with that of [Fe(III)(H₂O)₆]³⁺/[Fe(II)(H₂O)₆]²⁺ of 0.771 V. For the reduction of [Fe(III)(edta)]⁻, quite strong reductants are needed. Chelating ligands are existing in aged CESAR1, like ethylenediamine (EDA) (up to 0,46 wt.% or 77 mmol/kg in the test campaign) or oxalic acid (up to 0,12 wt.% or 14 mmol/kg), in sufficient amounts for the complexation of iron (maximum concentration 12 mg/kg or 0,21 mmol/kg), see Figure 16.

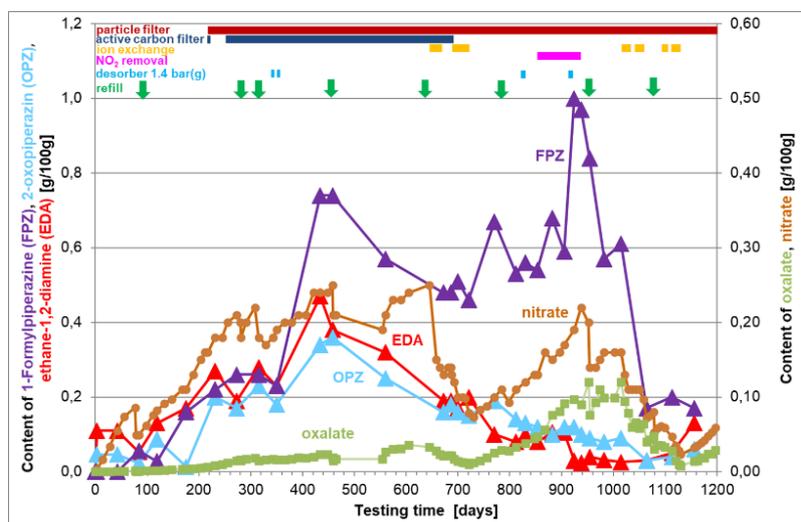


Fig. 16: Accumulation of the degradation products EDA: ethylene-1,2-diamine; FPZ: 1-Formylpiperazine; OPZ: 2-Oxopiperazine, nitrate and oxalate in CESAR1 during 1200 days of testing. Phases with elevated desorber pressure (blue bars, 1.4 bar(g) instead of 0.75 bar(g)) had no effect on the concentrations of EDA or oxalate, but on that of FPZ.

The EDA concentration reached a maximum concentration after ca. 430 days of operation and decreased linearly in the following campaign. The concentration of oxalate increased very fast after the anion exchange campaign, by factor of 100. Moreover, also complexes with positive charges are known with less voluminous ligands, like the basic iron acetate $[\text{Fe}(\text{III})_3\text{O}(\text{acetate})_6(\text{H}_2\text{O})_3]^+$. It is unknown if the chelate complexes given above or similar compounds are existing in the solvent. However, there is no doubt that the potentially as catalyst acting metals in the solvent are complexed and that their accessibility for reaction partners and their redox behavior are tuned by the ligands of the solvent matrix. A lower concentration limit for catalytically active metal ions from which the catalytic effect can be expected to be negligible cannot be specified and is not known. The solvent and the specific matrix of contaminants are more decisive for the degradation than the absolute metal ion concentrations. Additionally, it is extremely unlikely that industrial-scale application of amine-based CO₂ capture could be realized with metal-free solvents. Even if capture plants could be completely built from non-metallic materials, as investigated in LAUNCH in Task 2.3, already the pure technical amines will contain metal traces from their production processes and small metal or rust particles will enter the capture plant via the feed gas, so that metal ions will always be part of the solvent inventory. When cleaning of the solvent removes contaminants that hinder the effectivity of the catalysis, more damage than good is done. Excessive cleaning of the solvent would mainly waste valuable solvent.

Also the interaction of the metal ions and complexes with the active carbon (more exactly with the reactive binding chemical groups at the graphitic-like surface as -COO- or hetero atoms as N and S) can be interpreted as a special case of ion exchange. This emphasises the importance to consider the complete solvent matrix of the aged solvent for the prediction of degradation and optimisation of the solvent management. It can also explain the differences in the solvent behaviour in different capture plants, the impact of the construction materials of the capture plant and the dependence on flue gas properties. Operators of commercial capture plants should carefully analyse their individual operating and plant conditions depending on the solvent before they start to treat the solvent with the intention to reduce the formation rate of degradation products. Excessive reclaiming might have the opposite effect as intended.

4.2 Role of metal ions for the activation of oxygen

At first glance, the process of the oxidation of amines, but also of their degradation products which are accumulating in the CO₂ capture solvent, seems to be a simple reaction between the residual oxygen in the flue gas and the organic compounds. After reaching the thermodynamic equilibrium, it can be expected that in an alkaline solution dissolved HCO₃⁻, NO₃⁻ and H₂O are received as oxidation products, because of their strong negative Gibbs functions for formation of the compounds ($\Delta_f G^\circ_{molar}$ at 298.15K: H₂O_(liquid) - 237.1 kJ mol⁻¹; HCO₃⁻_(aq) -586.8 kJ mol⁻¹; NO₃⁻_(aq) -108.7 kJ mol⁻¹ [18]). However, these oxidation reactions do not proceed spontaneously and it is a matter of fact that the oxidation mechanism is highly complicated and comprises several elemental steps [19]:

- dissolution of the gaseous oxidizing species in the flue gas (e.g. O₂, NO, NO₂/N₂O₄, SO₃) into the solvent in the CO₂ absorber comprises diffusion of the oxidant from the gas phase to the flue gas-solvent interface,
- transfer of the species across the interface hydrolysis/ionization of the reactant in the solvent phase if possible,
- diffusion of the ionic and non-ionic species inside the solvent, and a wide range of possible chemical reactions inside the solvent.

An explanation why organic compounds in the solvent are not instantaneously oxidized by O₂ is the fact that organic substrates (amines, alcohols, ketones and acids) in the ground state all have closed shell electronic structures, and therefore are in a singlet state, while O₂ in the flue gas is a diradical (triplet O₂, ground state with the two unpaired electrons is the triplet spin state). Chemical interactions are governed by various selection rules, among which the ones due to Wigner formulate the constraint of overall spin-conservation [20]. For the reaction to occur, i.e. to preserve the spin, the transition state has to be a

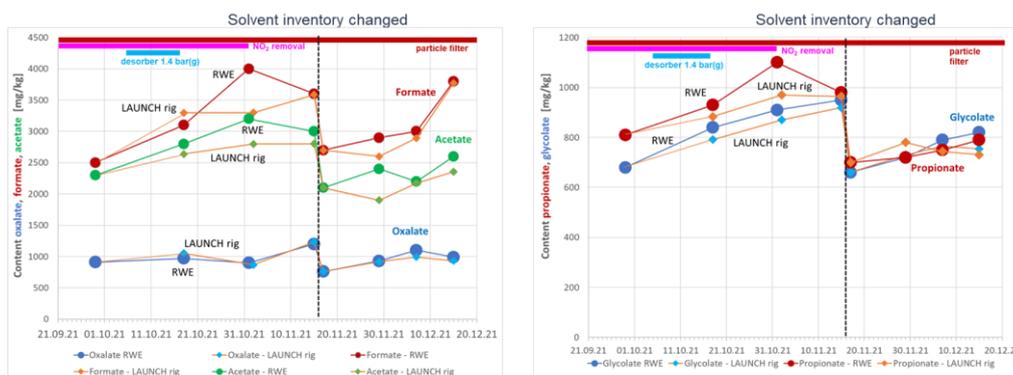
combination of the spins of the reactants and the products. That is the algebraic sum of the spins S of the reactants has to have at least one term in common with the algebraic sum of the spins of the products ($|S_{\text{Reactant}} \pm S_{\text{Oxygen}}| = |S_{\text{Product}} \pm S_{\text{Product2-Oxygen}}|$) [21,22]. An implication of these spin-selection rules is the inertness of $^3\text{O}_2$, if the other reactant and the product are spin singlets, as this reaction is spin-forbidden.

Reactions between organic substrates in singlet state with oxygen would be allowed by spin selection rules when the oxygen molecule is in an excited singlet state with paired electrons in different π^* orbitals. The necessary excitation energies are $156.9 \text{ kJ mol}^{-1}$ for $\text{O}_2(^1\Sigma_g^+)$ and $94.14 \text{ kJ mol}^{-1}$ for $\text{O}_2(^1\Delta_g)$ related to the ground state $\text{O}_2(^3\Sigma_g^-)$. Singlet O_2 can be photochemically produced by electronic energy transfer from photo-excited sensitizers or by thermolysis of peroxides. However, due to the lack of radiation with appropriate wavelength and dye-sensitizers, singlet oxygen seems to be irrelevant for the solvent degradation.

There are different options to circumvent the reaction barrier for triplet oxygen [24]. Metal complexes can provide spin-allowed pathways for reaction, due to their abilities to act as radicals with varied spin multiplicities if the number of electrons on a ternary complex (metal ion + amine + O_2) remains constant throughout the reaction [25]. Here, the reaction of $^3\text{O}_2$ with a paramagnetic metal $\text{LM}^{(n)+}$ ion (L represents complexation of metals like $\text{Fe}^{2+,3+}$, Cu^{2+} , $\text{Co}^{2+,3+}$, $\text{Ni}^{1+,2+,3+}$ by one or several ligands) can follow an activation route by sequential electron transfer summarized as: triplet oxygen $^3\text{O}_2$, superoxide O_2^- , peroxide O_2^{2-} and oxide O^{2-} . These reduction intermediates are weak acids and may exist protonated in the rich amine solution. Alternatively, free-radical formation or autooxidation can be catalyzed by metal ions. Here, a metal ion catalyzes the formation of free radicals, and thus the initiation of chain reactions that are responsible for the oxidative amine degradation. Moreover, the formation of hydroxyl radicals which react with the amine by hydrogen abstraction and formed by protonation of peroxides is catalyzed. Finally, the formation of organoperoxy radicals due to the direct one-electron oxidation by a metal ion can also be catalyzed [25].

4.3 Validation test on the effect of iron, nickel and copper on the degradation of CESAR1 using TNO's LAUNCH rig

An interesting, additional validation test regarding the effect of iron, nickel and copper on solvent degradation was possible by comparing the results from the pilot plant at Niederaussem with that of TNO's test campaign with the LAUNCH rig#2 (see Deliverable 5.2.2 "LAUNCH rigs: a validated tool for capturing solvent degradation behaviour"). The operation of the LAUNCH rig#2 started during the NO_2 removal test and already before the phase with elevated desorber pressure. The LAUNCH rig used the same original aged solvent, flue gas upstream the CO_2 absorber and process parameter settings as in the pilot plant (e.g. stripper temperature and pressure). Although some differences between the residence times of the flue gas and the solvent in the LAUNCH rig and the pilot plant exist, the analysis data for the solvent in both facilities show the same trends regarding the increase of oxidative degradation products and the accumulation of nitrate, chloride and sulfate in the solvent, see Figure 17.



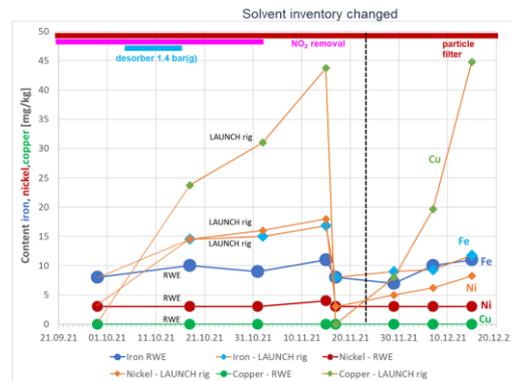


Fig. 17. Comparison between the increase of the concentrations of iron, nickel and copper, degradation products and the trace components in LAUNCH rig#2 and the capture pilot plant.

The concentrations and the increase rate of the concentrations of degradation products (formate, acetate, glycolate, propionate and oxalate) and trace components which are captured from the flue gas are almost exactly congruent for the LAUNCH rig and the capture pilot plant with the exception of the metal concentrations of iron, nickel and especially copper. In the solvent inventory of the LAUNCH rig a fast increase of the metals was determined. However, no effect on the degradation rate and the degradation mechanism results from this. This is another, independent proof that the absolute concentration of metal ions is not decisive for the degradation of the solvent, but must be discussed considering the solvent matrix and complex formation with the available ligands.



5 Conclusion

Solvent management aims at an efficient way to achieve the desired CO₂ capture rate with a minimum of solvent feed, energy consumption and operational issues, like foaming and fouling or precipitation caused by solvent contaminants. Additionally, the solvent consumption due to degradation and in connected with the removal of contaminants by applying reclaiming technologies should be reduced as much as possible. However, these goals of solvent management are not completely congruent. From a holistic perspective also solvent losses by emissions (solvent management always means also emission management) and the minimisation of waste streams and avoidance of corrosion of components of the capture plant must be analysed carefully.

The results from the campaign with CESAR1 at the capture plant in Niederaussem show that some suggested measures for solvent management need to be revised and cannot be generalized. It was demonstrated that the solvent matrix of the specific solvent and the accumulated contaminants which depend on the specific site conditions (flue gas composition, capture plant process configuration, plant materials, and operating characteristic) must be taken into consideration to better predict the degradation rate. Neither the solvent colour nor the metal concentration in the solvent are appropriate measures to control solvent management technologies or to describe the performance of the solvent. Ion exchange can effectively remove anions and cations from the solvent, but the consequential effects on the solvent degradation rate must be carefully considered. Based on the results of the campaign with CESAR1 the removal of ligands from the solvent which form complexes with metal cations can increase the degradation rate. More investigation is needed regarding the interaction of metal cations, which have the potential to act as a catalyst for oxygen activation and solvent degradation, and degradation products with capability to form complexes to avoid the opposite of the expected effect when activating solvent management technologies.

The trade-off between a simplified laboratory experiment, to focus on postulated core processes of solvent degradation, and the necessity to cover all relevant aspects of the real process configuration, comprises on one hand the risk of oversimplification and on the other hand the challenge to understand and correctly connect all necessary details. For that reason, it is essential to evaluate results from laboratory tests and artificial short-time test campaigns on solvent degradation based on the facts received from long-time testing with real flue gases. Without proof of the efficacy of specific solvent management technologies for individual solvents in the real application case, theories on effect mechanisms and derived guiding principles for solvent management in capture plant operation can be misdirected. The proposed guidelines should be reviewed. This can contribute to avoid waste of valuable solvent and resources and to optimize the environmental benefit from amine-based carbon capture. An intelligent combination of complementary laboratory experiments - making also use of solvent from real operation - with meaningful pilot plant tests of sufficient duration and innovative approaches, like the head-to-head operation of CO₂ capture plants of different size realized in the project LAUNCH, offer the opportunity to clarify the effects caused by the interventions of solvent management and effective key factors for solvent degradation in industrial CO₂ capture.

6 Literature

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