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Heat stable salts (HSS) removal by Electrodialysis: reclaiming of MEA used in post-combustion CO₂-capture

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Abstract

Heat-stable salts (HSS) are well-known degradation products in the acid gas removal technologies with alkanolamines, especially in the post-combustion CO₂ Capture processes. The traditionally applied HSS removal methods such as purging, filtration, distillation might be economically unattractive in the large scale post-combustion plant case. Electrodialysis could be an alternative method for solvent reclaiming with removal of electrically charged amine degradation products. This work presents the results of electrodialysis reclaiming concept tested under real operation conditions during pilot campaign at Heilbronn post combustion CO₂ Capture pilot plant. The HSS removal results and some process specific parameters are presented.

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1. Introduction

The degradation of amine-based solvents for CO₂ capture can cause increasing operational costs and maintenance as well as may lead to a long-term system performance deterioration [1]. Solvent degradation occurs through irreversible chemical reactions between the amine and components of the flue gas such as O₂, SO_x, NO_x, HCl etc., or with contaminants in the solvent itself, as degradation products by an oxidation process or as corrosion by-products

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[2]. Typical reaction products are heat-stable salts (HSS) which cannot be regenerated in the stripper, leading to a loss of solvent capacity and maybe other problems, e.g. corrosion, and foaming. Up to now, the petrochemistry has generally relied upon purging, filtration and thermal reclaiming in order to reduce the impact of the unwanted impurities [1, 3]. However, these proven technologies require the use of large volumes of chemicals and energy, in order to maintain a high solvent quality and a high CO₂-absorption capacity of the amine-based solvents. Due to different boundaries (such as oxygen) in the case of CO₂ capture of fossil power plants the electro dialysis (ED) could be an alternative, promising approach for solvent reclaiming [4-6] which allows the removal of unwanted compounds like HSS in the form of cations and anions from the alkanolamine stream.

As part of the EU-project OCTAVIUS a novel concept of ED-reclaiming has been scheduled to be demonstrated under real operating conditions at the post-combustion CO₂ Capture MEA pilot plant located at Heilbronn operated by EnBW AG. The pilot plant process scheme is shown on Figure 1 [7].

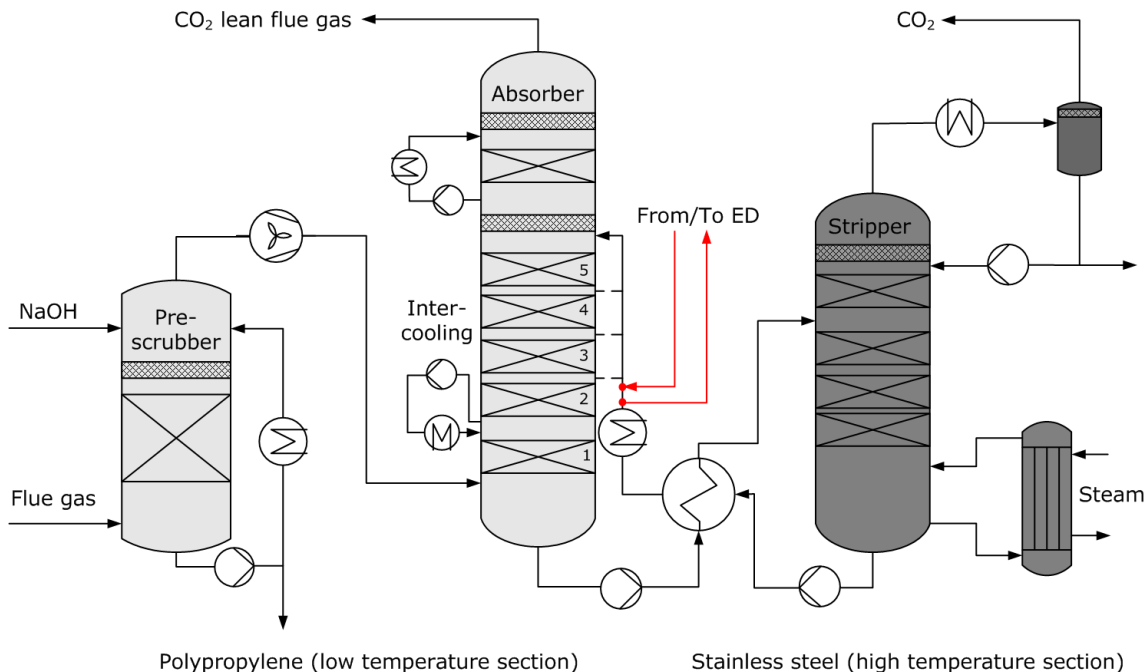


Figure 1. Post-Combustion CO₂ Capture Pilot Plant at Heilbronn [7].

A flue gas slipstream of about 1 500 Nm³/h is taken from the bituminous-coal fired unit 7 downstream of the power plant FGD. The flue gas first passes the pre-scrubber for further pre-treatment (acid gas scrubbing and cooling) before entering the proper CO₂ capture process. The pilot plant is designed to capture 7.2 tons of CO₂ per day at average CO₂-concentrations of the power plant and a capture rate of 90 % with 30% aqueous MEA solution.

This article presents first results of the ED-reclaiming concept with a pilot Electro dialysis Unit (EDU) on MEA solvent at the EnBW post-combustion CO₂ Capture pilot plant during the winter 2013/2014.

2. Program, technique and analytics

2.1-Solvent reclaiming with electro dialysis at Heilbronn capture plant

Electro dialysis unit was tested on a slip stream taken from lean solvent line after the lean cooler before entering the absorber (Figure 1). The lean MEA-solvent at 35°C with CO₂-loading about 0.2 mole CO₂/mole MEA was collected by an intermediate of 100 l tank, which was used as a feed tank for the EDU. The reclaimed solvent from

the EDU and the residue from 100 l feed tank were discharged back to the lean solvent line (Figure 1). The procedure of the feed tank refilling and ED-reclaiming was done for the solvent taken after 200 h, 400 h, 450 h, 535 h and 972 h of continuous pilot plant operation in order to investigate the HSS build-up and its influence on the EDU performance.

2.2 EDU description and testing

Based on lab-scale tests carried out during 1st OCTAVIUS project period [8], the novel concept of two-stage electro dialysis (ED) reclaiming was proposed in order to increase HSS removal rate and reduce concentrate volume. Two-stage method consists in sending the concentrate with high HSS content from 1st Stage electro dialyzer to the 2nd Stage electro dialyzer as a feed solution to be purified. Schematic and general view of two-stage EDU tested at Heilbronn pilot plant are shown in Figure 2.

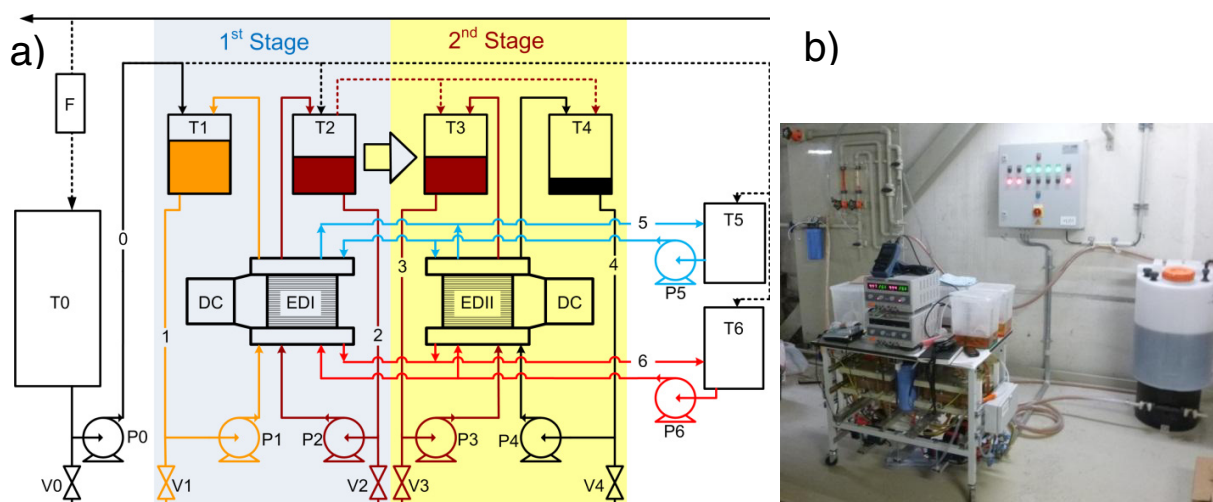


Figure 2. (a) Schematic and (b) General view of Two-Stage Pilot Electro dialysis Unit tested during MEA Campaign at Heilbronn.

The EDU contains two electro dialyzers: 1st stage and 2nd stage electro dialysis apparatus (ED I and ED II). Both electro dialyzers are identical and can also be used independently to double the feed solvent flow in case of using 1st Stage ED-reclaiming only. Each apparatus has the following parameters presented in Table 1.

Table 1. Electro dialyzers parameters

Parameter	Value
Overall membrane area, m ²	3
Voltage mode, V	45 – 80
Current mode, A	2 – 5
Number of Desalting cells	25
Number of Concentrate cells	24
Solvent flow, l/h	150
Linear liquid velocity, m/s	0.5
Cation exchange membrane MK40	
Anion exchange membrane MA41	

The EDU was operated by the following procedure (Figure 2). The feed solution was supplied by pump P0 from feed (intermediate) 100 l tank T0 via the line 0 to the 1st stage diluate (reclaimed solvent) tank T1 and electro dialyzer ED I until filling of approx.6 liter. Then the solution from the same line was supplied in varying amounts into the 1st stage concentrate tank T2 (approx.1l), catholyte tank T5 (approx.1l), and anolyte tank T6 (approx.1l) to provide the liquid flow through the lines 1-2 and 5-6. Initial lean solvent from the feed tank T0 was used as anolyte, catholyte and concentrate media for not making any perturbations of the process with other electrolytes. After turning on the pumps P1-2 and P5-6 the solutions from tanks T1-2 and T5-6 began to recirculate through lines 1-2 and 5-6 of 1st stage. The ED I was turned on with power supplier DC and started to remove the HSS from the solution in the T1 tank and line 1. The voltage mode was maintained at 1.5 V per membrane (70 – 80 V), so the current mode was controlled at a level not higher than 5 A (typically 2-4.5 A) to prevent the damage of power supplier DC. The solvent in the line 1 was treated by ED I for 1 hour, and the efficiency of ED-reclaiming was controlled every 5 minutes by checking of specific cubic conductivity (SCC) and temperature of the solvent in the tank T1. The diluate and concentrate liquid volumes were controlled by the scales on tanks T1-2. The diluate samples were being taken through the valve V1 every 10 minutes during the process. At the end the ED I was switched off and reclaimed solvent was discharged from line 1 via valve V1 back to the pilot plant line. The line 1 with tank T1 and the ED I were refilled by a new portion of initial solvent from the tank T0, and the ED-process was repeated. The above procedure of “filling-reclaiming-discharging” was repeated 4-5 times (4-5 cycles) to get a sufficient amount (approx. 5 l) of the concentrate in the tank T2. The concentrate samples were taken from the line 2 and tank T2 via valve V2 at the very end of whole process.

For the 2nd stage operation the 1st stage concentrate from tank T2 as feed solution was used. The concentrate was discharged from the line 2 and fed to tanks T3 (≈ 4 l) and T4 (≈ 1 l) After turning on the pumps P3-6 the solutions from tanks T3-6 began to recirculate through lines 3-6 of 2nd Stage. The ED II was turned on with power supplier DC and started to remove the HSS from the solution in the T3 tank and line 3. The voltage mode was maintained in the range of 45– 80 V in order to control the current at a level not higher than 5 A (typically 3-5 A) to prevent the damage of power supplier. The solvent in the line 3 was treated by ED II for approx..1.5 hour due to the higher HSS content. The specific cubic conductivity (SCC) and temperature of the solvent in the tank T3 was controlled every 5 minutes. The diluate and concentrate liquid volumes were controlled by the scales on tanks T3-4. The diluate samples were being taken through the valve V3 after 0, 45 and 90 minutes of the process. The concentrate samples were taken from the line 4 and tank T4 via valve V4 at the end of the process. Reclaimed solvent as well as 2nd stage concentrate were discharged from lines 3-4 back to the pilot plant.

2.3 Chemical analysis of samples

To validate ED-reclaiming with MEA solvent of the pilot plant under real operation conditions around 170 liquid samples were collected from both ED stages during the pilot EDU testing. Around 50 most relevant samples were chosen to be chemically analyzed for better understanding of ED-reclaiming process. The wide spectrum of species, such as HSS anions, heavy metals, alkali and alkali-earth metals, ammonia, nitrosamines, MEA and CO₂ were determined by the following methods:

- the anions of the HSS per ion chromatography (IC);
- the heavy metals and alkali/earth alkali concentrations by induced coupled plasma emission spectroscopy (ICP);
- ammonia by cationic IC;
- MEA and the CO₂-loading by acid titration.

3. Program, technique and analytics

In this section first observations and results are presented. In Table 2 the ranges of the operational parameters during the EDU testing (such as U, I, T, SCC) are presented in the form of “minimum value at the beginning – maximum value at the end”.

Table 2. The EDU testing regimes

ED - process	Solvent cases				
	(MEA solvent after . . . h of pilot plant operation)				
	200 h	400 h	450 h	535 h	972 h
	1 st Stage				
Number of cycles	4	5	5	5	5
Samples for HSS analysis are taken from . . . cycles of 1 st stage	1 st and 4 th	1 st and 5 th	n/a	1 st and 5 th	1 st and 5 th
Total voltage mode for all cycles, V	64 – 76	76 - 77	76 – 77	76 - 77	76 - 77
Total current mode for all cycles, A	2.6 – 4.7	2.4 – 4.7	2.4 – 4.2	2.3 – 4.6	2 – 3.7
Total temperature range for all cycles, °C	13.4 → 36.8	9.8 → 32.5	10.6 → 31.8	9.3 → 36.0	9 → 32.5
Total SCC range for all cycles, mS/cm	19.5 → 16.9	17.4 → 15.9	17.2 → 15.6	17.6 → 15.6	15.6 → 14.1
	2 nd Stage				
Number of cycles	1	1	1	1	-
Voltage mode, V	47 - 50	55 - 77	53 - 76	53 - 77	-
Current mode, A	4 - 5	3 – 5	3 - 5	3 - 5	-
Temperature, °C	19.8 → 38.1	10 → 36.6	13 → 38.7	10.7 → 37.3	-
Time of operation, days	2	3	3	3	2

3.1 HSS anions removal

The data on HSS removal are presented in Figure 3, where the dependence of total HSS content on ED-process time is shown. The total HSS content was calculated as the summarized concentration of formate, acetate, oxalate, glycolate, chloride, nitrite, nitrate, and sulphate anions. The extended basic data of chemical analysis for 535 h solvent case is presented in Table 3 as an example, though the similar analyses were performed for other solvent cases as well.

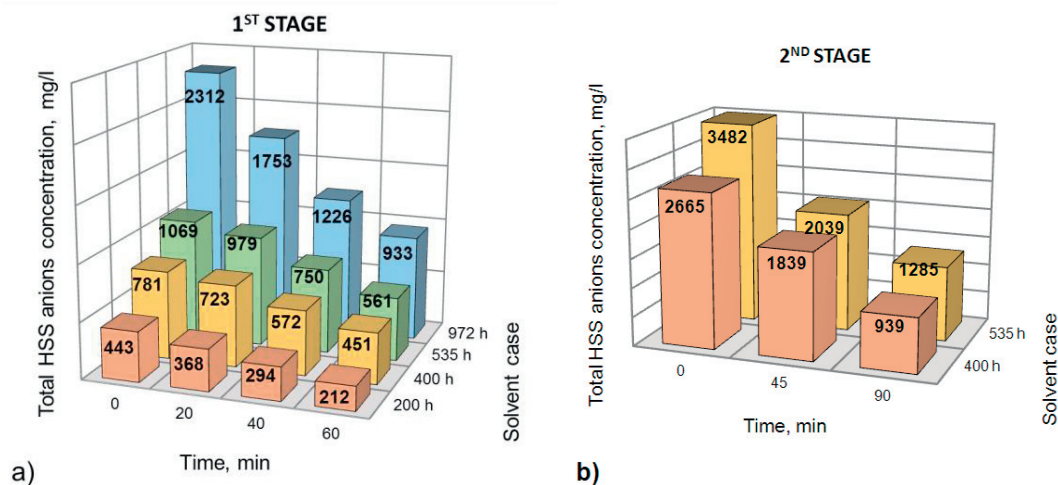
Figure 3. HSS removal during ED-process at: (a) 1st stage EDU testing; (b) 2nd stage EDU testing.

Table 3. HSS concentration before and after ED-testing for 535 h solvent case.

HSS anion	Concentration of HSS in diluate, mg/l			
	1 st Stage		2 nd stage	
	Before ED	After ED	Before ED	After ED
Formate	320	175	1 160	350
Acetate	110	60	350	190
Glycolate	65	40	205	105
Oxalate	114	69	270	140
Nitrite	0.5	2.9	7,1	2,9
Nitrate	145	40	600	55
Sulphate	310	170	820	420
Chloride*	4.4	3.8	70	22
Total	1 069	561	3 482	1 285

*- chloride concentration has been corrected due to ion-exchange process between solvent to be treated and ion-exchange membrane material initially charged with chloride ions.

As seen from Figure 3 and Table 3, the EDU reduces the entire spectrum of HSS anions up to 65% only for 1 hour at 1st stage and for 1.5 hour at 2nd stage, so the concept of ED-reclaiming is confirmed. The HSS removal degree and efficiency can be increased by increasing in membrane area under the equal conditions. Analytical results for the other components including heavy metals showed negligible changes of concentrations

3.2 Specific parameters of ED-reclaiming

Based on the analytical results and taking into account lab-scale results previously reported [8], dependencies of some specific parameters of process on initial total HSS concentration are presented on Figure 4. Specific concentrate volume was calculated as a volume of concentrate increased during ED-process divided by the overall mass of HSS anions removed. Specific energy consumption was calculated as a product of the average current value, average voltage value and time of the ED-process divided by the overall mass of HSS anions removed.

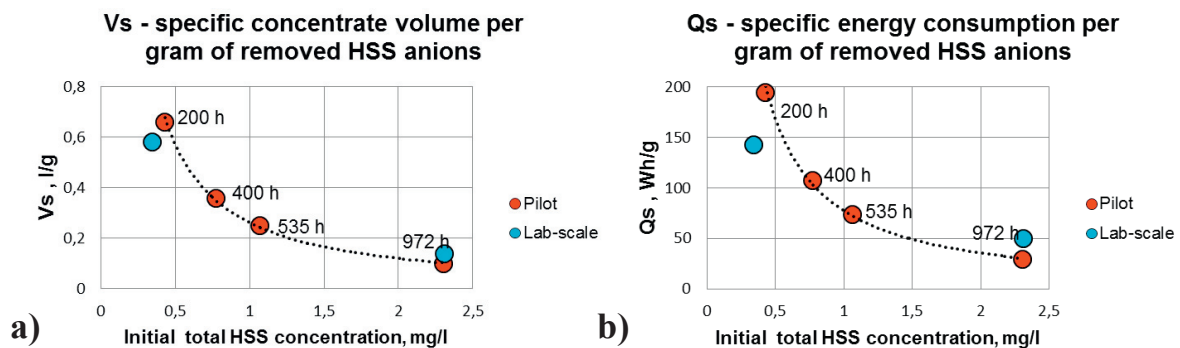


Figure 4. Specific parameters of ED-reclaiming process: (a) Specific concentrate volume; (b) Specific energy consumption.

As seen from Figure 4 the pilot EDU testing are in a good agreement with lab-scale results. The process becomes more effective from waste and energy consumption point of view at higher initial total HSS concentrations. Thereby it is very important to note that at the EDU launch moment the HSS concentration should be as high as possible, but less than the level that is critical for CO₂-Capture pilot plant operation from corrosion, foaming points of view. Such results can be basic for design of full-scale electro dialysis module for industrial solvent reclaiming.

3.3 EDU stability test

In order to evaluate stability performance of EDU, the control tests were carried out by using the same control solvent, which was MEA solvent taken from EnBW pilot plant at the very beginning of its running (0 h solvent case). Figure 5 represents the kinetics of ED-reclaiming of the control solvent at the beginning and at the end of the ED-reclaiming campaign.

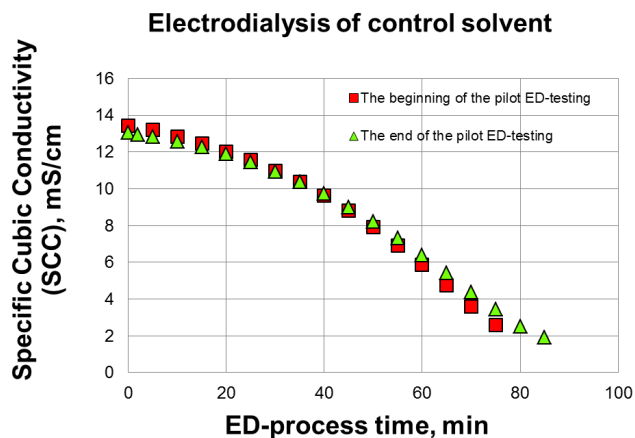


Figure 5. Kinetics of the ED-reclaiming of control solvent before and after pilot ED-testing.

The main indicator of ED process was the specific cubic conductivity (SCC) of solution. The data on kinetics consisted in decreasing of the SCC in time during the ED process. Figure 5 shows that the time depending curves (kinetics) for the control solvent are almost identical under the equal conditions. Thus, there is no noticeable, deteriorative impact of real MEA solvent compounds on the membrane performance of the EDU despite of the fact that such a solvent had up to 0.5 g/l of heavy metals (Fe, Cr, Ni) at the last time period.

3.4 Solvent colour shift

The visual control of the diluate and the concentrate at the end of 1st stage of EDU testing unexpectedly showed that a solvent colour shift takes place (see Figure 6), and that the reclaimed solvent is darker than the concentrate.

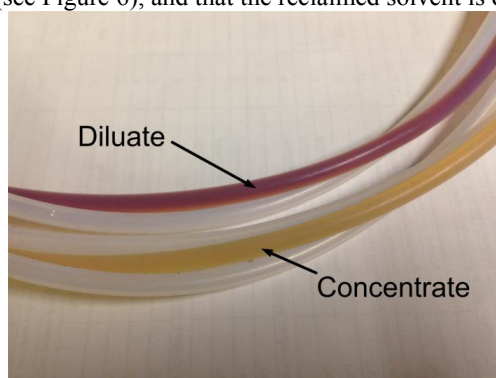


Figure 6. Colour shift example of solvent for 972 h solvent case after 5 cycles of 1st Stage ED-testing.

The reason for such a fact might be the porous structure of ion-exchange membranes with pore diameters up to 5 nm [9-10]. The coloured MEA degradation products with relatively high molecular weight could be rejected by

membranes and remain in the diluate part of the ED module.

4. Conclusions

In the present paper a two-stage ED-reclaiming concept for HSS removal from MEA solvent was described. The proposed concept was tested with specially designed electro dialysis unit under real operation conditions during a MEA campaign at Heilbronn pilot plant within the OCTAVIUS project. The pilot ED-testing showed a removal of HSS anions up to 65% for 1 h of EDU operation. The colour shift of diluate and concentrate streams can be attributed to rejection of coloured species by ion-exchange membranes during the operation. The pilot results are in a good agreement with lab-scale results.

Acknowledgements

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