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## Investigation of trace elements in the inlet and outlet streams of a MEA-based post-combustion capture process Results from the test programme at the Niederaussem pilot plant

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### Abstract

The first post-combustion capture pilot plant in Germany was constructed and commissioned in July 2009 at BoA 1 in Niederaussem, the most advanced and efficient lignite-fired power plant unit in the world, as part of the joint development programme of RWE Power, BASF and Linde that is aiming at a highly efficient CO<sub>2</sub>-scrubbing technology for power plants. The test programme at the pilot plant focuses not only on the energy demand for CO<sub>2</sub> capture, solvent stability and corrosion resistance of innovative materials but also comprises an extensive analysis programme regarding emissions. Therefore, the pilot plant is in particular equipped with an online gas-analysis system to continuously measure the composition of the inlet and outlet gas streams. In addition, an extensive sampling and measurement programme is being carried out with the aim of making up the balance of trace elements in the gaseous flows including components that are normally not determined. For the liquid drain streams, a wide range of physical and chemical data is collected in parallel with the analysis of the gas streams. This paper summarises the results of the measurement programme and the operational experience regarding solvent losses for the benchmark solvent monoethanolamine (MEA). Some of the results are compared with the outcome of other test facilities by way of example.

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*Keywords:* Post-combustion capture; amine scrubbing; MEA, emission, trace elements, material balance

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### 1. Introduction

Degradation of alkanolamines in post-combustion capture plants can result in an extensive amine loss and corrosion of the plant components – corresponding to higher operating and maintenance cost –, operational problems like foaming, increasing solvent viscosity and fouling as well as an environmental impact due to the emission of ammonia and aldehydes into the atmosphere. Besides the release of volatile degradation products, the emission of the solvent itself has to be taken into consideration. In their joint development project, RWE Power, BASF and Linde focused not only on determining the make-up rate of the solvent and the specific consumption per ton of captured CO<sub>2</sub> but on obtaining a broad and detailed understanding of the material flows between the capture plant and the environment.

The loss of active solvent in amine-based capture processes can be divided into two categories: physical solvent loss by entrainment and by the solvent vapour pressure; chemical solvent loss by degradation (oxidation) and solvent blocking (irreversible absorption of acid flue gas components and formation of heat stable salts). Although the oxygen and SO<sub>2</sub> content of the flue gas from coal-fired power stations are expected to be major factors for solvent degradation and the formation of heat stable salts, knowledge about the impact of trace elements is limited. The effects of a pre-scrubbing process step comprising the removal of acid components by sodium hydroxide addition to the recirculating water flow of the direct contact cooler on solvent losses are unclear so far.

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Especially for MEA work has been carried out both in laboratories and in pilot plant tests to understand the degradation mechanisms and parameters that influence the degradation rate [1-3]. At the pilot plant in Esbjerg, for example, the MEA consumption was quantified during two 500-hour tests. This was done by investigating the decrease in amine concentrations and the amounts of make-up MEA added. No solvent reclaiming was performed in Esbjerg and no corrosion or oxidation inhibitors were used. The minimum specific MEA consumption that could be determined was 1.4 kg/ton of captured CO<sub>2</sub>. But it was impossible to recalculate the MEA loss taking account of emissions and degradation products. The balance could not be closed.

Therefore, an extensive sampling and measurement programme aimed at making up the balance for trace elements flows and using MEA as solvent was carried out at the pilot plant in Niederaussem during a test campaign.

## 2. Pilot plant operation, sampling and analysis

### 2.1. Niederaussem pilot plant

The post-combustion capture pilot plant can capture up to 7.2 t of CO<sub>2</sub> per day from a flue gas slipstream of the lignite-fired 1,000 MW<sub>el</sub> BoA 1 unit at Niederaussem, which is equipped with state-of-the art electrostatic precipitators and a wet desulphurisation plant (FGD). The Niederaussem power station is ideally suited as a site for the post-combustion capture pilot plant because of its base-load operational characteristics. In comparison with hard coal-fired power plants in mid-load operation mode, this guarantees continuous testing and results that are easier to interpret. The pilot plant comprises all significant components of a full-scale PCC plant (without CO<sub>2</sub> compression) as shown in the process scheme in Figure 1. The basic absorber / desorber configuration is complemented by a number of additional components to improve performance. Upstream of the absorber, the flue gas is cooled down by the direct contact cooler to reach a gas temperature of 40°C at the absorber inlet. By adding sodium hydroxide to the recirculating water flow of the cooler, traces of acidic reacting components can be removed from the flue gas (pre-scrubber). The absorber is equipped with several beds and offers the option of bypassing beds to investigate the effect of different packing heights. Additionally there is the option of interstage cooling by using different side draws. The solvent cycle is fitted with a mechanical and an active carbon filter in a slipstream to remove possible particles (fly ash or gypsum from the FGD) or degradation products from the solvent flow. No reclaiming unit is installed at the pilot plant to observe the undisturbed degradation and accumulation velocity and to obtain a sufficient level of contamination in the solvent to allow its impact on process performance, solvent corrosiveness and emissions to be analysed.

The mechanical completion of the skid mounted pilot plant was finalized on 6 May 2009 followed by the commissioning phase and the start of the test programme in July 2009 [5, 6]. After some 5,000 hours of operation with MEA (30%-weight, no additives or activators) the comprehensive measurement campaign was carried out. The long-term test guaranteed a sufficient time for the solvent to degrade and to accumulate an adequate amount of degradation products as well as trace elements from the flue gas to obtain representative results.

The plant is in particular equipped with an extensive online gas-analysis system to continuously measure the composition of the inlet and outlet gas streams at four locations (flue gas at the pre-scrubber column inlet: CO<sub>2</sub>, CO, SO<sub>2</sub>, NO; flue gas at the absorber inlet: CO<sub>2</sub>, CO, SO<sub>2</sub>, NO, O<sub>2</sub>; CO<sub>2</sub>-lean flue gas downstream of the absorber outlet: CO<sub>2</sub>, CO, O<sub>2</sub>; CO<sub>2</sub> product stream: O<sub>2</sub>). Additionally, the total hydrocarbon (THC) concentration is measured in the outlet gas streams of the absorber and the desorber to estimate the loss of solvent and of degradation products as a function of the operating conditions.

### 2.2. Sampling and analysis methodology

The inlet and outlet streams of the overall pilot plant and of individual components (pre-scrubbing direct contact cooler, absorber, desorber) defined the battery limits for the balance as well as the sampling points as shown in Figure 1. Measurements of the gas composition comprised components that are normally not determined (SO<sub>2</sub> and SO<sub>3</sub>, NO and NO<sub>2</sub>, heavy metals, particles and organic compounds). For the liquid drain streams (condensate from the flue gas, condensate from the pre-scrubbing unit, the recirculating flow of the water wash section at the absorber head and condensate from the condensate separator downstream of desorber) a wide range of physical and chemical data was collected in parallel with the analysis of the gas streams (pH, conductivity, anions, cations, heavy metals, TOC/DOC, AOX, CSB, BSB).

The sampling, analysis and measuring of the individual trace elements and components of the gas streams was carried out by an accredited measuring agency. In general three individual measurements (each sampling period 30 minutes) were conducted in parallel at the four sampling points. The compounds MEA and ammonia were absorbed in HCl and subsequently in water and analysed by wet chemical analysis according to VDI Guideline 2467 (MEA) and VDI Guideline 2461 (ammonia). Ketones (acetone, methylethylketone) and alcohols were collected by adsorption and analysed according to DIN EN 13649. Organic Acids were determined by chromatography according to VDI Guideline 2457 and aldehydes by HPLC according to VDI Guideline 3862.

In addition, the liquid samples were taken simultaneously with the first gas sampling. Cations in the liquids were analysed according to DIN EN ISO 11885 as well as DIN 38406 and anions according to EN-ISO 10304 D 19 (sulphate, chloride, nitrate) and EN 26777 (nitrite). Physical data was determined according to DIN 38404 C5 (pH value) and DIN EN 27888 C8 (conductivity). The analysis of the liquids was carried out by RWE Power's accredited in-house laboratory.

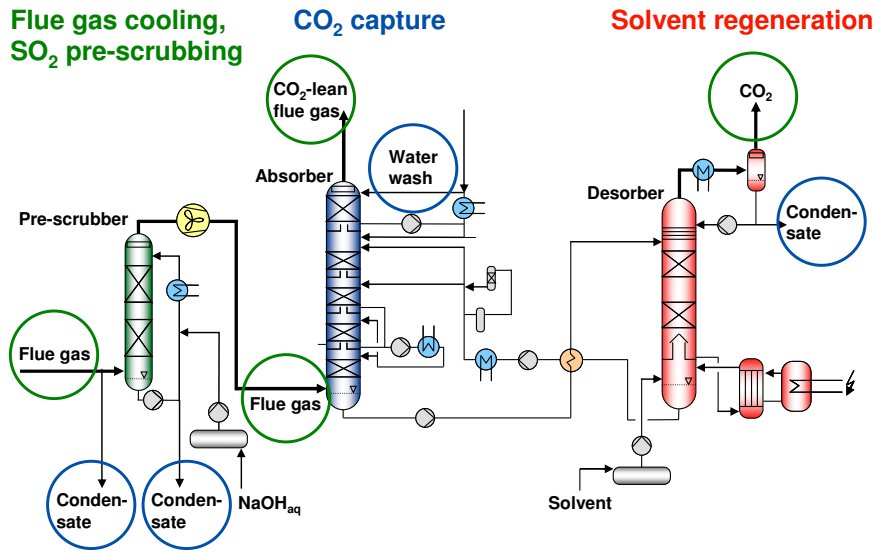


Figure 1: Sampling points in the balancing measurement campaign for the inlet and outlet streams in the process (green: gaseous flows; blue: liquid flows)

During the sampling phase the capture pilot plant was operated in stable mode with optimal operating parameter settings regarding specific energy demand of the process. Figure 2 shows the stable flows of the flue gas entering the capture plant and the treated gas flows leaving the process during the measuring campaign as well as the flow of the circulating solvent. This is a prerequisite for obtaining reliable and representative measuring and analysis results. Figure 3 additionally shows several important flue gas parameters. It gives an overview of the range of typical fluctuations and the slopes of changes in the flue gas.

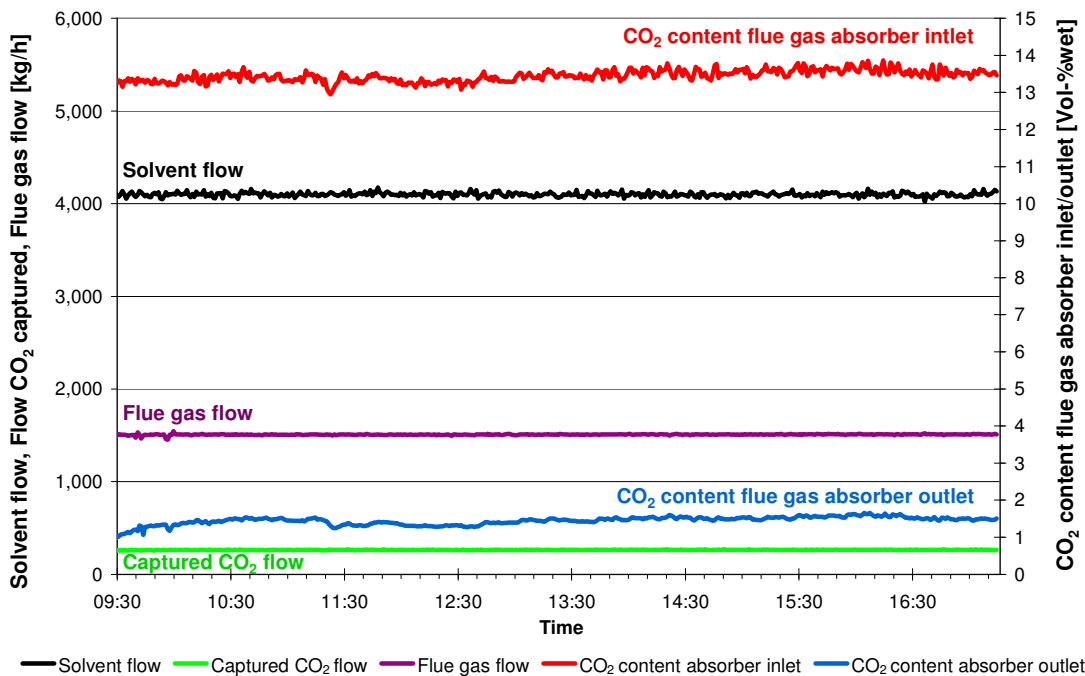


Figure 2: Stability of pilot plant operation during the sampling phase

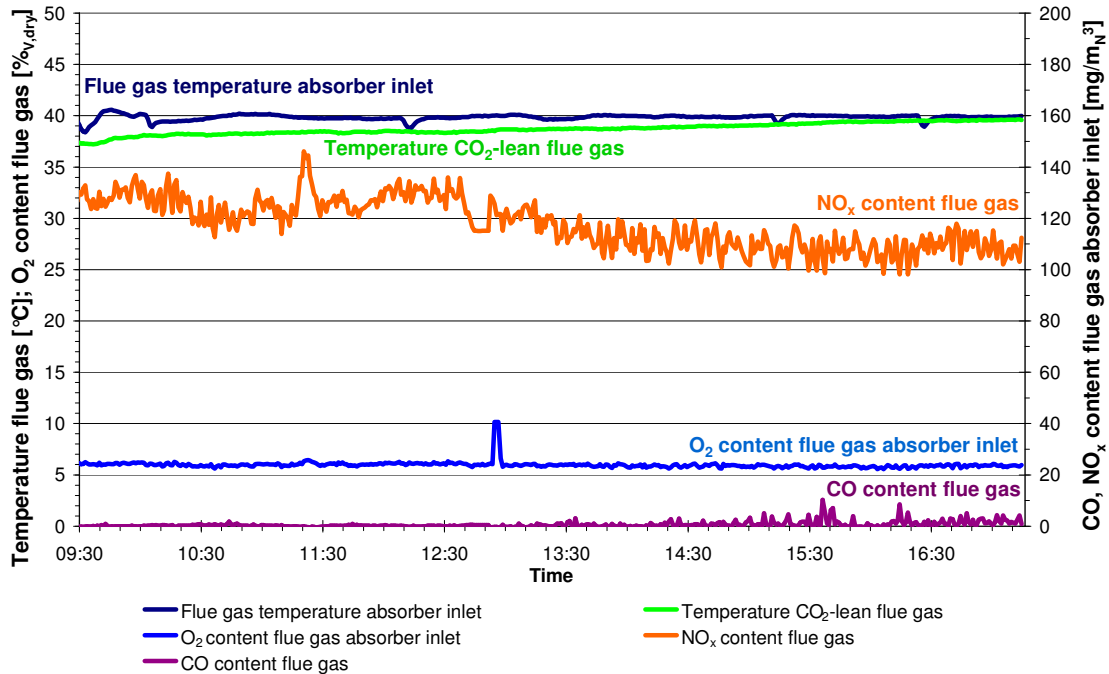


Figure 3: Time-dependent behaviour of the concentration of important flue gas compounds and temperatures during the sampling phase

During the total operating time with MEA a broad range of coal-related (composition, heating value), power plant-related (load, flue gas composition, emissions) and FGD-related (suspension properties, limestone properties, gypsum quality) parameters were monitored that might influence the performance of the capture process and degradation velocity.

### 3. Results

The basis for the determination of the material flows into and out of the capture process in connection with the solvent and its degradation products was the exact control of MEA make-up during the long-term test period over 550 hours, monitoring of the operating parameters and the emission measurements. The main focus of the measuring campaign at the end of the long-term test period was to determine the loss and make-up balance and to identify the sinks of MEA.

#### 3.1. Specific solvent consumption

The MEA loss and the corresponding need for solvent make-up during plant operation were determined taking account of the amine concentration of the solvent, the solvent filling levels of the capture plant components, the stripper condensate drain with traces of amine in it and also the amount of solvent removed from the process for analysis by sampling, which cannot be neglected at a test plant. The make-up flow of MEA into the process from the storage tank was also measured.

The solvent loss during the long-term test period was ascertained to 44 kg of MEA. At a captured amount of some 155 t of CO<sub>2</sub>, this is equivalent to a specific solvent consumption of approx. 0.29 kg/t<sub>CO<sub>2</sub></sub>. Thus, the determined MEA loss in the Niederaussem pilot plant is significantly lower than the values given in literature or found in test campaigns at the Esbjerg plant [4].

After this fundamental result it was necessary in the next step to investigate how much of the solvent loss is caused by emission of the solvent and how much by degradation.

#### 3.2. Emission of solvent

The measured concentration of MEA in the CO<sub>2</sub>-lean flue gas – relevant in particular regarding environmental aspects – was between 0.02 and 0.03 mg/m<sup>3</sup> (dry), which means an insignificant specific loss. The MEA loss via the captured CO<sub>2</sub> flow downstream of the stripper condenser was significantly higher with 8.1 to 11.8 mg/m<sup>3</sup>. Assuming that the measured concentration is representative for the total long-term test period this corresponds to a specific loss of less than 0.006 kg/t<sub>CO<sub>2</sub></sub>. Although this loss is also very small it was higher than expected. In a pit stop following the measuring campaign it was found that the reason for this was the malfunction of a bubble tray at the desorber top that could easily be corrected. The general result is a low loss of amine solvent via the gas flows.

### 3.3. Emission of degradation products

The most important loss of MEA via gas streams out of the process is connected with the oxidation product ammonia. The  $\text{NH}_3$  concentration in the  $\text{CO}_2$ -lean flue gas was 26.9 to 46.6  $\text{mg/m}_N^3$ . Assuming that the degradation of one MEA molecule causes the release of one  $\text{NH}_3$  molecule, this corresponds to a MEA loss of between 0.32 and 0.56  $\text{kg/t}_{\text{CO}_2}$ . The  $\text{NH}_3$  content of the captured  $\text{CO}_2$  was only 1.1  $\text{mg/m}_N^3$ , which is equivalent to a MEA loss of less than 0.003  $\text{kg/t}_{\text{CO}_2}$ .

Other degradation products play only a secondary role. In the  $\text{CO}_2$ -lean flue gas the concentration of acetaldehyde was less than 0.2  $\text{mg/m}_N^3$  (<0.001  $\text{kg/t}_{\text{CO}_2}$ ) and of acetone 0.5 to 1.0  $\text{mg/m}_N^3$  (0.004 to 0.008  $\text{kg/t}_{\text{CO}_2}$ ). In the captured  $\text{CO}_2$  the concentration of acetaldehyde was between 11.6 to 12.9  $\text{mg/m}_N^3$  (0.008 to 0.009  $\text{kg/t}_{\text{CO}_2}$ ) and of acetone 0.3 to 1.0  $\text{mg/m}_N^3$  (<0.001  $\text{kg/t}_{\text{CO}_2}$ ). All other determined component concentrations were smaller than the measurement accuracy.

In summary it can be said that within a measuring uncertainty of only 10% the MEA balance can be closed for the capture process. This is an excellent result in the light of the challenge of determining traces in material flows under real power plant operating conditions and not in an idealised laboratory environment. The approach to calculate the solvent loss during the long-term test from three individual measurements of the emissions contains some uncertainty. But the results match and justify the approach.

In the last balancing step it was examined whether the concentration of organic residual molecule fragments after the dissociation and release of  $\text{NH}_3$  would coincide with the corresponding amount of  $\text{NH}_3$  that was measured in the gas streams.

### 3.4. Degradation products in the solvent

Solvent samples were analysed at the BASF laboratory (titration, GC/MS, HPLC). The most important degradation products accumulated in the solvent during 5,000 hours of operation were acetate with a mass-related content of 1.8 %, formate 0.2 % and oxalate <0.1 %. More complex degradation products such as 1-(2-hydroxyethyl)imidazolidone-2, which is not formed by oxidation of MEA but simply by reaction of  $\text{CO}_2$  and MEA, were detectable but even at the end of the MEA test campaign reached only very low concentrations and are negligible for the balance. The same applies in particular to carbamate polymerisation.

During the long-term test period the specific loss of MEA caused by acetate formation was 0.203  $\text{kg/t}_{\text{CO}_2}$ . Taking into consideration other organic degradation products in the solvent (0.024  $\text{kg/t}_{\text{CO}_2}$  were quantified), losses by solvent sampling and by gaseous MEA fragments leaving the process, the specific loss by degradation products in the solvent within a measuring uncertainty of only 10% corresponds with the measured specific MEA consumption and within a 15% uncertainty range with the amount of emitted  $\text{NH}_3$ .

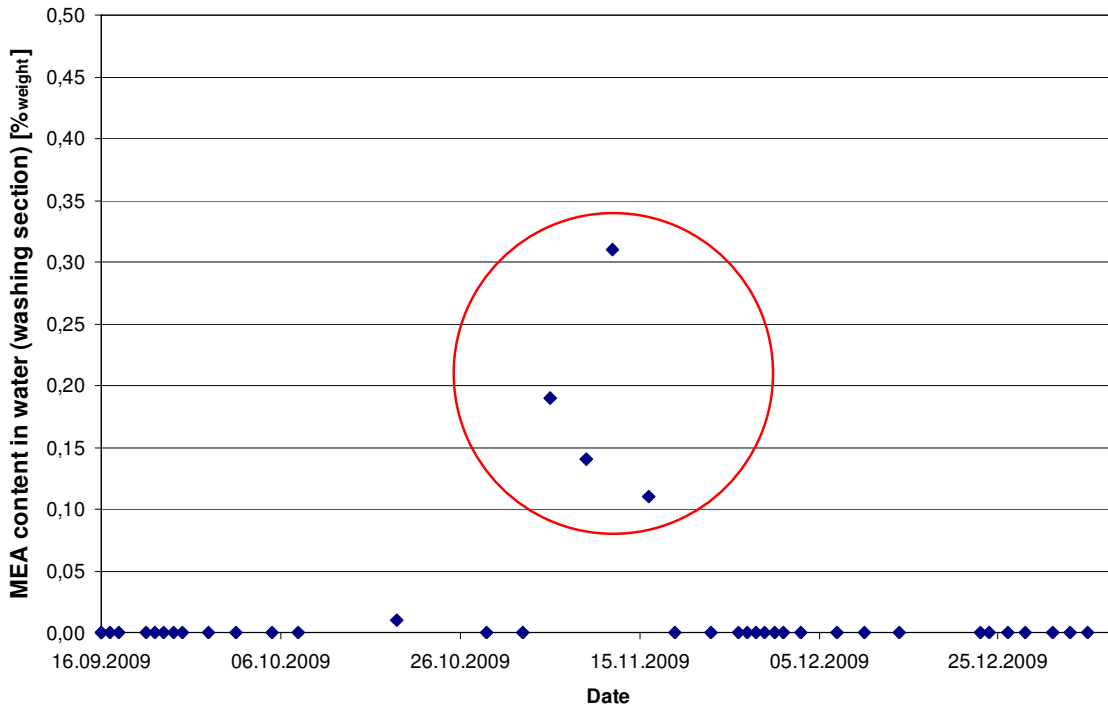
Table 1 summarises the MEA mass balance for the capture process regarding solvent make-up, loss by emission of MEA and degradation products as well as accumulation of MEA-derived fragment compounds in the solvent.

Table 1: Long-term test period parameter and balancing of the specific loss of MEA:

<b>Parameter</b>		
Testing time	[h]	550
Captured $\text{CO}_2$	[t]	155
<b>Specific MEA consumption (estimated accuracy +/-10%)</b>	<b>[kg/t<math>_{\text{CO}_2}</math>]</b>	<b>0.284 (0.256 – 0.312)</b>
<b>Balance of the loss of MEA</b>		
<b>Equivalent specific MEA loss by MEA emission and volatile degradation products (measuring the gas phase concentration)</b>		
Specific MEA emission	[kg/t $_{\text{CO}_2}$ ]	0.006
Specific MEA loss in connection with $\text{NH}_3$ ( $\text{CO}_2$ -lean flue gas)	[kg/t $_{\text{CO}_2}$ ]	0.32 - 0.56
Specific MEA loss in connection with $\text{NH}_3$ (captured $\text{CO}_2$ )	[kg/t $_{\text{CO}_2}$ ]	0.003
Specific MEA loss in connection with acetaldehyde	[kg/t $_{\text{CO}_2}$ ]	0.004 - 0.008 $\text{kg/t}_{\text{CO}_2}$
Specific MEA loss in connection with acetone	[kg/t $_{\text{CO}_2}$ ]	<0.001 $\text{kg/t}_{\text{CO}_2}$
<b>Sum (estimated accuracy +/- 10%)</b>	<b>[kg/t<math>_{\text{CO}_2}</math>]</b>	<b>0.334 – 0.578 (0.301 – 0.616)</b>
<b>Equivalent specific MEA loss by degradation products in the solvent</b>		
Specific MEA loss in connection with acetate	[kg/t $_{\text{CO}_2}$ ]	0.203
Specific MEA loss by other compounds, sampling and volatile products	[kg/t $_{\text{CO}_2}$ ]	0.024
<b>Sum (+/- 15%)</b>	<b>[kg/t<math>_{\text{CO}_2}</math>]</b>	<b>0.227 (0.193 – 0.261)</b>

#### 4. Influencing emissions by process conditions

Although the determined level of MEA emission via the CO<sub>2</sub>-lean flue gas stream was very low, it was observed how the variation of the capture process conditions can further reduce the environmental impact. At the top of the absorber an additional packed bed is installed to backwash possible solvent losses due to volatility and entrainment (water wash section; Figure 1). Normally a small make-up water flow is added to the pump around in the water wash section to close the water balance of the pilot plant. Figure 4 shows the concentration of MEA in the pump around water flow of the water wash section, which effects in the end the MEA emission. Under standard operational conditions the concentration of MEA in the pump around was very low. But for non-optimised operating conditions of the pilot plant the MEA content in the wash water increased significantly. For these outliers either no make-up water was fed to the wash section or the wash section was operated at an elevated temperature. Although the make-up water rate of that plant is under standard conditions very low - about 15 kg/h, which is typical for such units operating at ambient pressure - this small amount of water helps significantly to reduce the MEA content in the water of the wash section, and the emission of MEA consequently. For one of the outliers two main-facts caused the higher MEA content in the wash water. Firstly, the temperature of the wash water was about 5°C higher than under the standard conditions and secondly, the lean loading of the solvent at the top of the absorber was lower. Due to the lower lean loading the volatility of MEA was increased. The higher solvent loading the lower is the amount of non-ionic MEA, which reduces the content of MEA in the gas phase, consequently. The lower lean loading was caused by a reduced circulation rate of the solvent in comparison to the optimized operation conditions, but with the same CO<sub>2</sub> removal rate.



a much higher effect than the doubling of the liquid load from 15 to 30 m<sup>3</sup>/m<sup>2</sup>h, where nearly no difference of the MEA emission was calculated. The simulation predicts that the temperature of the wash water influences the retention of MEA significantly more than the addition of make-up water. The simulations considered also that a lower temperature of the treated gas reduces as well the make-up water rate, but nevertheless this effect is overcompensated by the lower temperature, e.g. based on the simulation result it is expected that cooling down the wash water only to 50°C instead of about 40 °C doubles the MEA emissions. Finally the performance of such a wash section with a water pump around can be improved by an appropriate design (bed height, sizing of pump and cooler) as well as by optimised process conditions (flow rate, temperature, make-up water). The theoretically and empirically identified optimal parameters can be directly transferred into the design and the operation of a full-scale capture plant.

## 5. Conclusion

A reliable appraisal of the degradation and emission tendency of a solvent requires testing of the capture process with real flue gas and under real power plant operating conditions. The test campaign with MEA at the post-combustion capture pilot plant in Niederaussem resulted in an outstandingly low consumption of MEA in comparison with literature data and results from other test facilities. The MEA consumption and the measured losses of MEA by emissions and accumulation of degradation products in the solvent could be balanced, which confirms the extraordinary options for testing and assessing all aspects of capture process performance in Niederaussem. It is likely that the reason for the low MEA degradation rate is the removal of some contaminants from the flue gas by the pre-scrubbing unit. More detailed investigations into the responsible cause-and-effect relationship are ongoing. The results can contribute to the optimisation of the process design of a large-scale post-combustion capture plant to reduce emissions of amine and NH<sub>3</sub> traces and to minimize the environmental impact.

## 6. Acknowledgements

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