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## Novel concept for emission control in post combustion capture

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### Abstract

Aker Clean Carbon has developed a novel emission control concept consisting of the combination of anti-mist design and a pH controlled polishing step. This concept was tested at a 200 kg/h CO<sub>2</sub> capture test facility operating on flue gas from a coal-fired power plant. The tests demonstrated large removal of volatile compounds like ammonia and alkyl amines. In addition, the tests indicated that formation and emission of amine mist could nearly be eliminated. Thus, all in all the tests indicated that Aker Clean Carbon's novel emission control concept can virtually eliminate emissions of amines and other alkaline constituents from amine based post combustion capture plants.

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### 1. Introduction

In recent years the focus on potential emission of amines and amine degradation production from post combustion capture (PCC) plants has increased substantially. In particular emissions of amines and harmful degradation products such as nitrosamines and nitramines are a concern. Direct emissions of nitrosamines and nitramines can largely be avoided by selecting amine solvents that do not form stable nitrosamines and nitramines at the conditions prevailing in the capture process. However, emission of compounds containing amine groups are still a concern as these compounds may undergo nitrosation in the atmosphere to form nitrosamines or nitramines. For this reason it has been a key priority for Aker

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Clean Carbon to develop emission control technology that can secure low emissions of amines to the environment. Amines and other degradation products may in principle be emitted from post combustion plants by three different mechanisms: Gas phase emission, entrainment of liquid droplets as well as mist (aerosol) formation. Where conventional emission control technologies such as water wash sections and demisters have been an integral part of the design of amine based CO<sub>2</sub> capture plants for years, typically no abatement technologies have been implemented to deal with amine mist. Amine mist may for instances be formed in the CO<sub>2</sub> absorber when vapor phase amine is absorbed in fine mode water droplets (mist). Because of the tiny particle size of the mist particles they tend to penetrate wash sections and conventional demisters. Thus, there is a risk that the conventional emission control technologies may not be sufficient to meet the stringent emission limits that are likely to be imposed on large-scale PCC plants.

In this work, a novel concept for reduction of emissions of amines and amine degradation products from amine based PCC plants is presented. The concept consist of a novel absorber design to prevent mist formation as well as a pH controlled polishing step to eliminate emission of alkaline constituents with the treated flue gas. The concept has been demonstrated at Aker Clean Carbon's 200 kg/h mobile CO<sub>2</sub> capture facility on real flue gas from a coal-fired boiler. The tests were conducted with 30% MEA solution as well as novel amine solvents.

### **Nomenclature**

ACC	Aker Clean Carbon
DMA	Dimethylamine
DiEA	Diethylamine
EA	Ethylamine
MA	Methylamine
MTU	Mobile Test Unit

## **2. Test facility and Test Programme**

### *2.1. Mobile Test Unit*

All the test results reported in this paper are based on test campaigns conducted at Aker Clean Carbon's Mobile Test Unit (MTU). The MTU is a custom-built mobile test CO<sub>2</sub> capture facility, which can be used to capture CO<sub>2</sub> from different industrial flue gases. The facility is used to verify new design features and solvents, and operates in an industrial environment during long-term testing. The facility is designed for easy transport and hook-up, which means that it can be transported to different sites.

The MTU was commissioned in 2008 and since then several test campaigns have been conducted at different test locations and with different solvents [1, 2]. Amongst others verification of emission control technology and emissions has been an area of attention [1, 2]. Process improvements and new technology have been implemented in the MTU on a continuing basis.

A schematic 3D illustration of the MTU is shown in Figure 1. The design of the MTU is based on conventional amine absorption/desorption process with full packing height absorber and desorber

columns. Several novel features are installed such as ACC's Energy Saver and Emission control technology. The MTU absorber is fitted with two pump-around water wash sections in series, whereof the upper wash can be operated as an acid wash. Extensive instrumentation is implemented at the MTU and all on-line signals are logged in historical databases.

During 2011 the MTU was modified to include Aker Clean Carbon's Anti-Mist Design to significantly reduce emissions of amine mist. Key design data and specifications of the MTU are shown in Table 1.

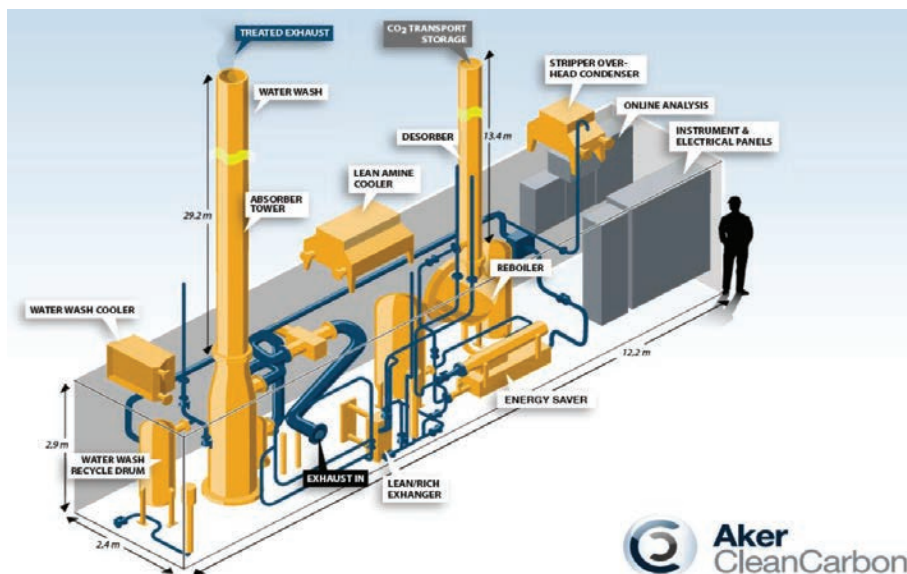


Figure 1. Schematic 3D illustration of the MTU of Aker Clean Carbon.

The MTU is equipped with a permanent FTIR online emission monitoring system from Gasetm™. The FTIR is connected via heated sampling lines (180°C) to sampling probes at the absorber inlet (downstream DCC), absorber outlet and desorber overhead condenser outlet. The FTIR is calibrated for a list of standard flue gas pollutants, e.g. CO, CO<sub>2</sub>, SO<sub>2</sub>, HCl, NO, NO<sub>2</sub>, NH<sub>3</sub>, as well as MEA and ACC solvent amines.

Table 1. MTU Key design data and specifications

Parameter	Design value	Unit
Max flue gas capacity	1000	Nm <sup>3</sup> /h
CO <sub>2</sub> capture (10% vol CO <sub>2</sub> )	200	kg/h
CO <sub>2</sub> capture efficiency	≈90	%
Absorber diameter	0.40	m
Absorber packing height	Up to 18	m
Desorber diameter	0.32	m
Desorber packing height	8.0	m
Solvent circulation	0-3.6	m <sup>3</sup> /h
Number of washing stages	2	-

## 2.2. Test program

For the tests reported in this paper the MTU was located at Southern Company's Ernest C. Gaston Electric Generating Plant/National Carbon Capture Center (NCCC) in Wilsonville, Alabama, USA. The MTU was operated on flue gas from unit 5, which is a modern coal-fired boiler equipped with DeNO<sub>x</sub>, ESP and FGD plants. Data is reported from the following two MTU test campaigns:

- Campaign 1: End June to mid-November 2011. Approx. 2200 hours operation with ACC novel Solvent
- Campaign 2: End November to mid-December 2011. Approx. 500 hours operation with 30% MEA

Amongst others, the scope of the test campaigns has been to test and validate Aker Clean Carbon's novel emission control concept, which consists of a novel absorber design to prevent amine mist formation and a final pH-controlled wash stage to eliminate emissions of volatile alkaline compounds.

## 2.3. Test procedures

*Acid wash test:* A 2-day acid wash test was conducted near the end of Campaign 1 after the solvent had been in operation for approximately 2000 hours. During the acid wash test, the MTU was operated at fixed settings meaning that the flue gas flow rate, the CO<sub>2</sub> capture percentage and the temperature of the wash sections were maintained at constant values. No cooling was applied in the upper washing stage in acid wash mode in order to avoid condensation of water from the flue gas and thereby bleeding of acid wash water. Because of heat loss to the surroundings, a small net condensation of moisture from the flue gas occurred in the acid wash section resulting in liquid accumulation in the acid wash water drum during the test.

Acid was supplied to the acid wash circulation loop as 10 %w/w sulfuric acid solution by the means of a dosing pump. Because the primary pH meter controlling the acid supply was out of order, the dosing pump was operated in manual mode. The pH of the wash water was manually monitored by an alternative pH indicator, which was not connected to the data acquisition system. After commencing acid addition, the pH dropped after a small delay from above 8 to below 4-5. The pH was maintained below 5 until in the afternoon the following day. Due to relatively high inventory in the acid wash relative to the concentration of alkaline compounds in the flue gas, the pH stayed below 5 for several hours after the acid dosing was stopped. Samples of liquid from the acid water wash drum wash collected before and after the test.

*Anti-mist tests:* The anti-mist design in the MTU has been implemented in a flexible way that allows switching between conventional mode and anti-mist mode operation within a time frame of say 15-60 minutes. In this way it has been possible to directly demonstrate the benefits of the anti-mist design on amine emissions. For the main part of Campaign 1, the ACC anti-mist design was implemented in a provisional manner, which only allowed for relatively short periods of anti-mist mode operation at the time. In the end of Campaign 1 additional modifications were implemented, which allowed for longer periods of anti-mist mode operation during Campaign 2.

Prior to switching from conventional to anti-mist mode operation and vice-versa, the MTU was held in steady state operation. This means that the main operational parameters such as reboiler temperature, desorber pressure, flue gas and solvent flow rates were maintained at fixed values. However, at some

stage in the campaign (30 November) the flue gas flow to the absorber had to be reduced as the reboiler duty was insufficient to reach the target CO<sub>2</sub> capture efficiency (90%). The MTU was operated with two water wash stages during the entire campaign, except under the acid wash test described above. During the entire test campaign the emissions of amine and ammonia from the absorber were monitored by the online FTIR system.

*Online FTIR emission monitoring:* The MTU's permanent FTIR system was used for online monitoring of amine emissions from the absorber during both test campaigns. The FTIR technique has the advantage that the sample gas is measured at actual conditions without any preconditioning, hence reducing the risk of analyte loss. To avoid condensation of water in the sampling system and the analyser, the FTIR gas cell and the sampling lines are heated to 180°C. This also has the advantage that any target compounds that is present as mist or droplets will be evaporated and analysed. Hence, the FTIR monitor provides the total content of the different analytes in the flue gas. A draw-back of the FTIR technique is the interference from water vapour which results in relatively high detection limit depending on the actual component to be measured and the flue gas composition. The experience from the MTU is that reliable NH<sub>3</sub> and amine readings down to approximately 1 ppmv can be obtained.

*Manual emission measurements:* Manual emission measurements were conducted at the outlet of the MTU absorber (stack) before and during the acid wash test to quantify the emissions of ammonia and volatile amines. A sampling train consisting of a short stainless steel probe connected to 4 midjet impingers in series was applied. The 3 first impingers were filled with 0.1 M sulfamic acid as absorbent and the 4<sup>th</sup> was left empty. The impingers were placed in an ice bath. Flue gas was drawn through the impingers by the means of a battery driven pump. A gas meter was used to quantify the sampled amount of flue gas. Typically each measurement lasted for approximately 1 hour. After completion of a measurement, the probe and sampling lines were flushed with ultra-pure water and the wash water and impinger solutions were sent for analysis. The samples were analyzed by LC-MS and GC-MS.

### 3. Results and Discussion

#### 3.1. Reducing emission of ammonia and volatile amines (Effect of pH controlled water wash)

Ammonia and alkyl amines are typically formed during oxidative degradation of solvent amines [3, 4]. These compounds are not captured to significant degree in traditional water wash stages because of their low solubility in alkaline solutions i.e. water wash. The water washes will therefore quickly saturate and the amounts of ammonia and alkyl amines emitted from the process will equal the amounts produced from degradation. Depending on the stability of the solvent, the flue gas source as well as the operating conditions, the emissions of ammonia and alkyl amines may be relatively significant. The emissions of these compounds may to some extent be kept at low levels by maintaining high solvent purity and thereby low degradation. However, in some cases excellent solvent management may not be sufficient to secure low emissions of ammonia and alkyl amines.

Recorded ammonia emissions during the trials with acid wash are shown in Figure 2. The MTU was operated at steady conditions for the duration of the test. Acid dosing to the upper washing stage was commenced around 9:00 on 16 November according to the procedure described in section 2.3. It is observed from Figure 2 that the ammonia emissions reported by the MTU's FTIR analyser decreased from around 3-4 ppmv before acid dosing to ≈1 ppmv during acid dosing. The ammonia emission of ≈1 ppmv is close to the detection limit of the FTIR system, implying that the true ammonia emission may be

significantly below 1 ppmv during acid dosing. Figure 2 furthermore indicates that the ammonia emission starts to increase up towards the starting level after the pH has increased above 5, clearly demonstrating the effect of acid dosing.

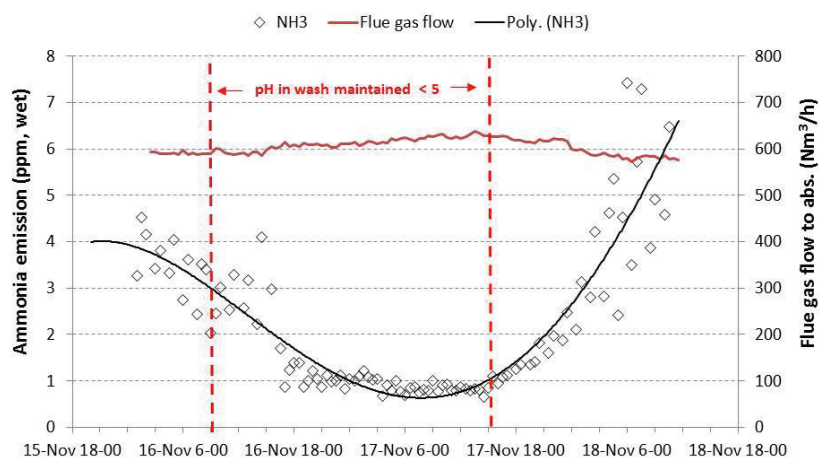


Figure 2. Impact of acid wash on ammonia emission trend from absorber by FTIR.

As mentioned in section 2.3, manual measurements of ammonia emissions were conducted. However, the measurements were not successful as it was later discovered that the chosen impinger absorbent (0.1 M sulfamic acid) dissociated to produce ammonia, hence preventing quantification of the ammonia absorbed from the flue gas. Nevertheless, the acid wash water was analyzed for ammonia before and after the test as shown in Table 2. A mass balance around the acid wash indicates an average capture of  $\approx 4$  ppmv ammonia which is relatively similar to the ammonia emission indicated by the FTIR during periods without acid wash operation. This indicates high ammonia removal efficiency of the ACC acid wash system.

Table 2. Ammonia content and liquid inventory of acid wash water

Sample	Ammonia	Inventory
Acid wash water 16 Nov 8:50 (start)	27 mg/L	97 L
Acid wash water 17 Nov 13:30 (end)	213 mg/L	210 L
Average flue gas flow:	$\approx 630 \text{ Nm}^3/\text{h}$	
Estimated $\text{NH}_3$ capture from flue gas:	$\approx 4 \text{ ppmv}$	

The baseline ammonia emission of 4-5 ppmv is rather low compared to what is previously observed at the MTU with MEA solvent [1] and coal derived flue gas indicating that the oxidative degradation rate of the novel solvent is substantially lower than that of MEA. In particular considering that the solvent has been operated with coal flue gas for approximately 2000 hours prior to the acid wash test.

Table 3 shows the emissions of simple (i.e. volatile) alkyl amines measured at the MTU operating respectively with and without acid wash. While some scatter is observed between the different

measurements without acid wash, all the four alkyl amines are positively detected although in low amounts. On the other hand, it appears from Table 3 that the emissions of alkyl amines are below the detection limits in both measurements conducted on 16 November under acid wash conditions. A mass balance around the acid wash (similarly as for ammonia in Table 2) indicates that the individual alkyl amines are accumulated in the wash corresponding to capture rates in the range of 0.003 to 0.01 mg/Nm<sup>3</sup>. This is fairly consistent with the manual emission results provided in Table 3 and shows that acid wash is an effective to reduce emissions of volatile alkyl amines.

Table 3. Emissions of simple alkyl amines (mg/Nm<sup>3</sup>) with and without acid wash

	Date & Time	Settings	DMA	MA	EA	DiEA
Test 1	14. Nov 15:45	No acid wash	0.0027	0.0031	0.0054	0.0031
Test 2	15. Nov 9:30	No acid wash	0.0018	0.0021	0.005	0.0029
Test 3	15. Nov 15:40	No acid wash	0.0025	0.0058	0.012	0.0058
Test 4	16. Nov 14:10	Acid wash	< 0.0013	< 0.0022	< 0.0004	< 0.0004
Test 5	16. Nov 16:25	Acid wash	< 0.0011	< 0.0019	< 0.0004	< 0.0004

### 3.2. Reducing mist borne amine emissions through ACC's Novel anti-mist design

Figure 3 shows the amine emissions from the MTU during a 2-day period under Campaign 1, where the operation was alternating between conventional mode and anti-mist mode. Also the CO<sub>2</sub> content in the flue gas to the absorber is shown. It appears from Figure 3 that an abrupt drop in amine emission occurs as the MTU operation is shifted into anti-mist mode. After some time in anti-mist mode, the amine emissions tend to stabilize at close to zero or at the detection limit of the FTIR system. When the MTU is switched back into conventional operation mode, the amine emissions are increasing abruptly back to the starting level. As seen from Figure 3 this emission behaviour can be repeated by changing the operating mode. Judging from the level of amine emissions (20-35 ppmv) during conventional operating mode it is clear that the ACC anti-mist design offers significant improvement. The observed amine emission in conventional mode is much higher than expected according to vapor-liquid equilibrium data for the water-amine system. This clearly indicates that the emission of solvent amine is mist controlled. It should be stressed that the level of mist generation and mist emission will be very dependent on the characteristics of the flue gas. Flue gases that are relatively free from particulate matter such as flue gases derived from natural gas or light gasoil are not expected to show similar potency with respect to mist formation. Also the extent of amine mist generation will most likely be very dependent on the type and performance of the flue gas cleaning devices installed upstream the CO<sub>2</sub> capture plant.

During periods where the MTU is operating in conventional mode, Figure 3 shows that changes in the flue gas CO<sub>2</sub> concentration typically trigger changes in amine emission. The CO<sub>2</sub> concentration of the flue gas changes as result of load changes at the power plant. It is speculated that load changes at the power station may influence the concentration and or nature of nuclei in the flue gas to the MTU and thereby affect the extent of amine mist generation. Figure 3 also shows that the decrease in amine emissions during switch to anti-mist mode is not coupled to changes in the CO<sub>2</sub> inlet concentration, i.e. power plant load changes, as this remains relatively stable during the transitions.

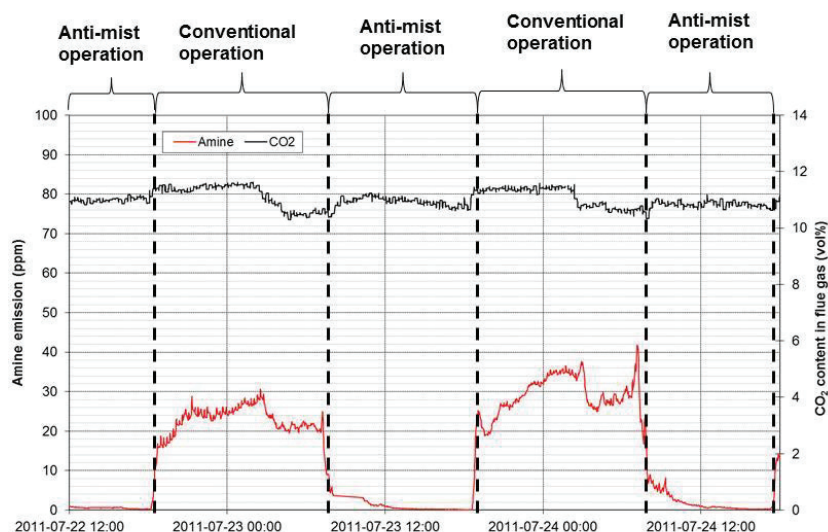


Figure 3. Emission of solvent amines during operation alternating between conventional and anti-mist mode.

The ACC anti-mist design was also tested for a longer period with 30% MEA solvent during Campaign 2, which is shown in Figure 4. As seen in Figure 4, the MTU operation is switched to the anti-mist mode after about five days of operation and kept in this mode for about 6 days before it is switched back to the conventional mode. During conventional mode operation Figure 4 shows significant fluctuations in the MEA emission and relatively high emission 10-50 ppmv with even higher peak values. Similar as with the novel solvent in Campaign 1, the vapor-liquid equilibrium data for the MEA-water system cannot explain the high MEA emission and the peaky emission behavior during seemingly stable operating conditions. This also indicates that the MEA emission is primarily mist borne. When the MTU is switched to anti-mist mode it appears from Figure 4 that the emission of MEA drops down to near zero or to the detection limit of the FTIR. The emission of MEA stays close to 0 ppmv for the entire period where the MTU is operated in the anti-mist mode. Again, this clearly demonstrates the efficiency of ACC's anti-mist design and further demonstrates that it works on different amine solvents. Considering the fluctuations in the CO<sub>2</sub> content of the flue gas, i.e. power plant load variations, it seems that changes in MEA emission are coupled to power plant load variations as previously explained. Nevertheless, Figure 4 reveals that the MEA emission is hardly affected by load variations during anti-mist mode operation.

Figure 4 furthermore shows that the emission of ammonia varies from below 10 to above 40 ppmv during Campaign 2. The higher emission is observed initially after which a declining trend is observed until the last five days of the campaign where the emission is increasing again. The reason for this behavior is not completely known. However, the ammonia emission seems not affected to a large extent by the anti-mist mode of operation. This is in accordance with expectations as the volatile nature of ammonia makes the ammonia emission volatility driven. In general the ammonia emission during the MEA campaign is significantly higher than during the campaign with ACC Solvent i.e. Figure 2, indicating lower oxidative degradation of ACC solvent.



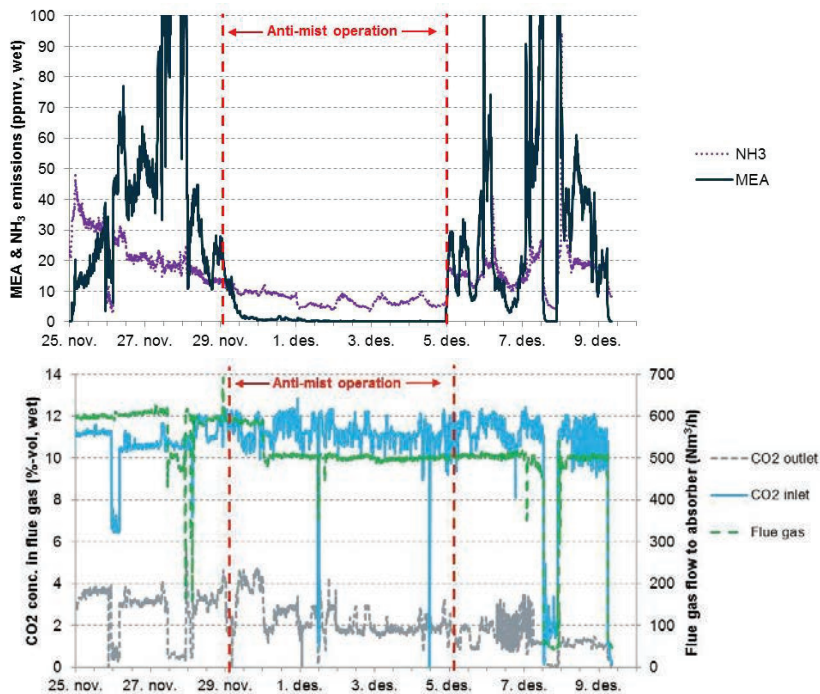


Figure 4. Emissions of NH<sub>3</sub> and MEA as well as flue gas flow and CO<sub>2</sub> content in and out of absorber during Campaign 2.

The findings from the MTU testing in this work demonstrate that the combination of ACC's anti-mist design and pH controlled polishing step are strong measures to achieve very low emissions of both mist borne compounds (amines) as well as of volatile degradation products like ammonia and simple alkyl amines.

#### 4. Conclusion

In this work a novel emission control concept developed by Aker Clean Carbon was tested at a 200 kg/h mobile CO<sub>2</sub> capture unit. The emission control concept consists of the combination of anti-mist design and a pH controlled polishing step. Tests were conducted with flue gas from a coal fired power plant and with novel solvent as well as with 30% MEA. The tests showed large removal of volatile compounds like ammonia and alkyl amines. In addition, the tests indicated that significant emissions of solvent amines in the form of mist may occur with conventional emission control technology. However, the formation and emission of amine mist could nearly be eliminated with Aker Clean Carbon's anti-mist design. Thus, all in all the tests indicated that Aker Clean Carbon's novel emission control concept can virtually eliminate emissions of amines and other alkaline constituents from amine based post combustion capture plants.

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