Report

WP 4 in the project: CCM TQP amine 6 – Emission Quantification and Reduction

Author(s)
Earl Goetheer and Eirik F. da Silva

SINTEF Materials and Chemistry
Process Technology
2012-01-30

Report

WP 4 in the project: CCM TQP amine 6 – Emission Quantification and Reduction

CO$_2$ capture,
Emission control,
Amines

VERSION
2

DATE
2012-02-07

AUTHOR(S)
Earl Goetheer and Eirik F. da Silva

CLIENT(S)
Gassnova SF, Dokkveien 10, N-3920 Porsgrunn, Norway. Contract No: 257430180

CLIENT'S REF.
Morthen Helgøy

PROJECT NO.
801862

NUMBER OF PAGES/APPENDICES:
20 + 5 Appendices

ABSTRACT
Identification of other emission reducing technologies
This report describes the preliminary work focused at the reduction of emissions from post combustion capture plants. An assessment is made dealing with the available technologies. Two technologies, acid wash and electrostatic precipitator, have been examined in more detail. The main advantage for the acid wash technology is that low emissions of amines and ammonia present in the vapour phase can be obtained. The impact of an acid wash step on aerosols should be further investigated. However, research done in other projects suggests that an acid wash system can have an impact on aerosol based emission of MEA. The main advantage of an electrostatic filter is that a high reduction of aerosols can be obtained. A drawback is the relatively high capital expenditure. It seems that upon combining both systems a very environmentally friendly capture plant can be designed.

PREPARED BY
Eirik F. da Silva

SIGNATURE

CHECKED BY
Thor Mejdell

SIGNATURE

APPROVED BY
Ole Wærnes

SIGNATURE

REPORT NO.
F21929

ISBN

CLASSIFICATION
Restricted

CLASSIFICATION THIS PAGE
Restricted

Document history

VERSION	DATE	VERSION DESCRIPTION
1	2011-11-28	Draft
2	2012-02-07	Final

Contents

1 Introduction

This report is focused on possible emission reduction technologies related towards nitrosamines and aerosol formation in post combustion capture processes. The basis of this report is five Memos on this subject. These Memos can be found in the appendices.

In the paragraphs below the some important conclusion dealing with the pilot plant measurements are discussed. In Chapter 2, technical economical consideration is discussed for a selected number of reduction options. Chapter 3 is focused on a tentative work-plan for the development of the reduction technologies.

1.1 Aerosol formation

From the pilot plant campaign it can be concluded that the MEA emissions after one water wash stage is in the order of 85-180 mg/Nm^3 (dry). This is far higher than expected by ASPEN modelling. Moreover, using a Brownian Demister Unit (BDU) the emission dropped to 1 to 4 mg/Nm^3. [1]

If the MEA was predominantly present in the gas phase, the BDU would not be effective. Therefore, the high efficiency of the BDU indicates that the relatively high content of MEA present in the treated flue gas is due to aerosol formation. In Appendix 5 some reasons for this aerosol formation is given. Summarized, the presence of SO_3/H_2SO_4 aerosol[2] and dust particles in the flue gas coupled with the temperature bulge in the absorber leads to the formation of aerosol of the condensation type. A matter of debate is where the majority of these aerosols are formed, in the absorber section or in the wash section. It could be argued that the rate of temperature decline and the absolute temperature (i.e. this is related with the vapour pressure of MEA) are key parameters in determining aerosol formation. Methods to reduce the formation of aerosols can be basically summarized (see also Appendix 3 and 5) to:

- Reduce temperature bulge or rate of temperature decline (e.g. by intermediate cooling, second water wash)
- Reduction of heterogeneous nuclei (e.g. by improved flue gas clean-up)
- Reduction of absolute temperature in the absorber

However, even by employing the above mentioned strategies there will always be a chance of substantial MEA emission by aerosol formation. It is of importance to note that aging of the solvent will probably have limited effect on the aerosol formation. This is based on the fact that the main route of aerosol formation is by condensation and not by mechanical entrainment. The latter is influenced by the surface tension of the absorption liquid. The surface tension can be reduced by the aging of the solvent.

The main methods for post removal of aerosols would be:

- Electrostatic precipitation
- Filtration (e.g. Brownian diffusion demisters)

---

[1] Report: WP 1 and 3 in the project: CCM TQP amine 6 – Emission Quantification and Reduction, by Herman Kolderup, Kai W. Hjarbo, Arjen Huizinga, Ilse Tuinman, Kolbjørn Zahlsen, Kai Vernstad, Astrid Hyldbakk, Torunn Holten, Hanne M. Kvamsdal, Peter van Os, Earl Goetheer

[2] This is typical for a coal fired power-plant. This would not be applicable for a natural gas fired power-plant.

For the cleanup of the gas from components present predominantly in the vapour phase such as ammonia, an acid wash would be the most preferred option.

In the report here below the main focus is on the technical and economic assessment of an additional acid wash and electrostatic precipitator processes.

1.2 Nitrosamine emission

In this test period also the nitrosamine emissions have been measured before and after the BDU. Traces of NDELA, N-morpholine and NDMA has been observed at both positions[3]. Typically, around 100 ng/m^3 of NDELA, 20 ng/m^3 NMOR and 10 ng/m^3 of NDMA. It is of importance to note that the efficiency for the removal of nitrosamine by the BDU is limited. The order of removal efficiency is NDELA (~70%) ›NMOR (~50%) ›NDMA (~10%). Based on the properties of these components, the order of efficiency is logical. NDELA is the most polar molecule and has the lowest vapour pressure.

Comparing the BDU efficiency for the removal of MEA with the efficiency for the removal of nitrosamine, the conclusion can be made that the nitrosamines are present in the vapour phase. Typical options for lowering the emission would be using additional water wash steps. An acid wash would not lead to a substantial improvement of the removal of nitrosamine compared with a more traditional water wash. The reason for this is that the relevant nitrosamine does not have an alkaline nature.

However, it is of importance to examine the possibility of a sink for the nitrosamine present in the absorption liquid. When using water wash with a recycle of the wash water to the absorber, the level of nitrosamine in the absorption liquid will increase. Therefore, a method for the reduction of nitrosamine is perhaps needed. Therefore, the behaviour of the nitrosamine during reclaiming is important. This should be measured and compared with the formation rate of nitrosamine and the wash efficiency as function of the nitrosamine concentration. Another quite interesting option is to destroy the nitrosamine by using an acid wash with a strong oxidizer or using techniques such as an UV-destruction.

Both options are discussed further in Chapter 2.

---

[3] No nitrosamines have been measured above the measuring threshold in the BDU-catch.

Reduction technologies

In this chapter the merits of the following technologies are discussed:

- Additional acid wash
- Electrostatic precipitator
- UV-treatment
- Alternative reduction technologies: Hydrogenation and Adsorption

1.3 Additional acid wash

With an additional acid wash is meant that next to a conventional water wash, a second acid wash section is used. This acid wash section is typically operated at the same temperature as the acid wash incoming flue gas. Typically, this acid wash will be operated in a pH range of 2 to 4. The system can be operated with a bleed and feed system to keep the quality of this acid wash constant or by a periodically complete replenishment of the acid wash liquid.

It is of importance to note that the acid wash liquid can be modified with strong oxidisers, for the destruction of organic components (e.g. $KMNO_4$). However, the efficiency of such a system needs to be evaluated with experiments. Moreover, the impact of the degradation products originating from the destruction of organic components should be investigated.

The main components of the envisaged system are:

- Structured packed bed (2-4 meter bed height)
  - o Detailed calculations are needed to evaluate the appropriate height. Structured packing (similar type as the packing of the regular washing section) is recommended to reduce pressure drop. The packing material should be corrosion resistant.
- Liquid distributor
  - o This can have a conventional design
- Liquid collector
  - o It is of importance that no acid should enter the sections below. With an appropriate design this should not be an issue
- Circulation pump
- Holding vessel

The above named elements will create that the absorption column will be 6 to 10 meter higher. The holding vessels will create a higher overall footprint.

1.3.1 Additional CAPEX

To estimate the additional needed CAPEX, the 430 MW natural gas fired NGCC plant from the EBTF (European Benchmarking TaskForce) is used. For this system (with only one normal wash section) using MEA as solvent, the following CAPEX has been estimated:

S. No.	Equip. Name	Nos.	Price in M€	%
1	Flue gas blower	1	2,27	7%
2	Absorber fluid pump	1	0,29	1%
3	Absorber column	2	13,7	40%
4	Lean-rich exchanger	1	0,78	2%
5	Lean Liquid cooler	1	0,58	2%
6	Reboiler	2	1,45	4%
7	Stripper	1	1,46	4%
8	Stripper fluid pump	1	0,29	1%
9	Condenser	2	1,46	4%
10	Condenser fluid pump	1	0,02	0%
11	Cooling water pump	2	0,44	1%
12	Storage vessel	1	0,25	1%
13	CO2 compressor	1	8,9	26%
14	Scrubber	1	0,527	2%
15	Flue gas direct contact cooler	1	1,225	
16	Flue gas cooling water cooler	1	0,342	
17				
18				
19				
20				
Total Cost of Purchased Equipment =			**34**	

Total Direct Costs (D)

S. No.	Description	Total in M€
1	Purchased Equipment	34
2	Erection, Steel structures and Painting	17
3	Instrumentation and Controls	3
4	Piping	7
5	Electrical Equipment and Materials	4
6	Civil works	3,7
7	Start up costs (solvent)	1,5
Total Direct Plant Costs (TDPC)		**70**

Indirect Costs (I)

S.No.	Description	Total in M€
1	Yard Improvements	1,0
2	Service Facilities	1,4
3	Engineering and Supervision	5
4	Buildings	3
Total Indirect Costs (I)		**10**
Fixed Capital Investment, TDPC + I =		**80**
5	Capital Fee	2
6	Contingency	9
7	Working Capital (WC), % of TCI	**3**
Total Capital Investment (TCI)		**94**

Legend

Direct Costs

1) Instrumentation and Controls	*Taken as*	*9*	*% of the purchased equipment c*
2) Piping	*Taken as*	*20*	*% of the purchased equipment c*
3) Electrical Equipment and Materials	*Taken as*	*12*	*% of the purchased equipment c*
4) Civil works	*Taken as*	*11*	*% of the purchased equipment c*
5) Erection, Steel structures and painting	*Taken as*	*49*	*% of the purchased equipment c*

Indirect Costs

1) Yard Improvements	*Taken as*	*1,5*	*% of the Total direct Costs*
2) Service Facilitites	*Taken as*	*2,0*	*% of the Total direct Costs*
3) Engineering, Supervision and construction	*Taken as*	*6,5*	*% of the Total direct Costs*
4) Buildings (Including Services)	*Taken as*	*4,0*	*% of the Total direct Costs*

Further costs

Contingency	*Taken as*	*10,0*	*% TCI*
Capital fee	*Taken as*	*2,0*	*% TCI*
Working capital	*Taken as*	*3,0*	*% TCI*

For this case, this would mean that both absorption columns would be equipped with an additional acid wash scrubber of 4 meter packing height and with a diameter of 13 meter. This would lead to an extension of the column with approximate 10 meters. This would add and additional 3 million euro. Next to this, costs have to been taken into account for two pumps and holding vessels. A rough

PROJECT NO.
801862

REPORT NO.
F21929

VERSION
2

7 of 44

estimation would be an additional 300 keuro. This would increase the total cost of purchased equipment with 10% (from 34 to approximate 37 million euro).

1.3.2 Additional OPEX

Operational costs will be the additional energy needed to overcome the pressure drop over the acid wash, the chemicals needed and the disposal of the waste stream. In a follow-up, upon determination of the conditions of the acid was liquid, this can be estimated more precisely.

1.3.3 Preliminary conclusions and open research questions

Based on the analysis performed in this Chapter and in the relevant appendices, it can be concluded that using acid wash can lead to a more robust performance of the capture plant, with limited cost. Therefore, it is recommended to further investigate this option for the reduction of alkaline components such as ammonia and organic components such as nitrosamines and nitramines. A limitation is that this technique would be efficient for components present in the gas phase and not as present in aerosols. However, within TNO indications have been found that an acid wash can be applicable also for the reduction of MEA present in aerosols. Kinetic aspects can be of importance.

The following aspects need to be studied in more detail

- Selection of acid

- Determination of optimal acid concentration (pH)

- Mass transfer

In case of using oxidative conditions in the acid wash section, the following aspects should also be addressed:

- Selection of oxidant

- Determination of typical degradation products

- Mass transfer

- Impact on degradation products

Based on the above aspects, a process design can be made, which can be used for a detailed technical and economic analysis.

From an HSE point of view, this can be considered as mature technology. Therefore, significant amount of HSE related information can be found dealing with acid wash scrubbing. The challenge would be in the addition of strong oxidizers. This warrants attention on this topic in the next phase.

1.4 Electrostatic precipitators

Electrostatic precipitators (ESP) (see Figure 2-1) are well known in the power sector. The basic principle is that particles are given an electrical charge by using a corona. An electrical field forces the charged particles to the walls. The layer of particles on the walls can be knocked loose and removed from the precipitator. Continuous washing with water can also be used (WESP). Electrostatic precipitators are capable of removing particles above 1-2 micrometer. These devices can have a high design efficiency (99-99.9%). A precipitator collects particles most easily when the particle size is coarse. The generation of the charging corona in the inlet field may be suppressed if the gas stream

has too many small particles (less than 1 µm). Very small particles (0.2 - 0.4µm) are the most difficult to collect because the fundamental field-charging mechanism is overwhelmed by diffusion charging due to random collisions with free ions.
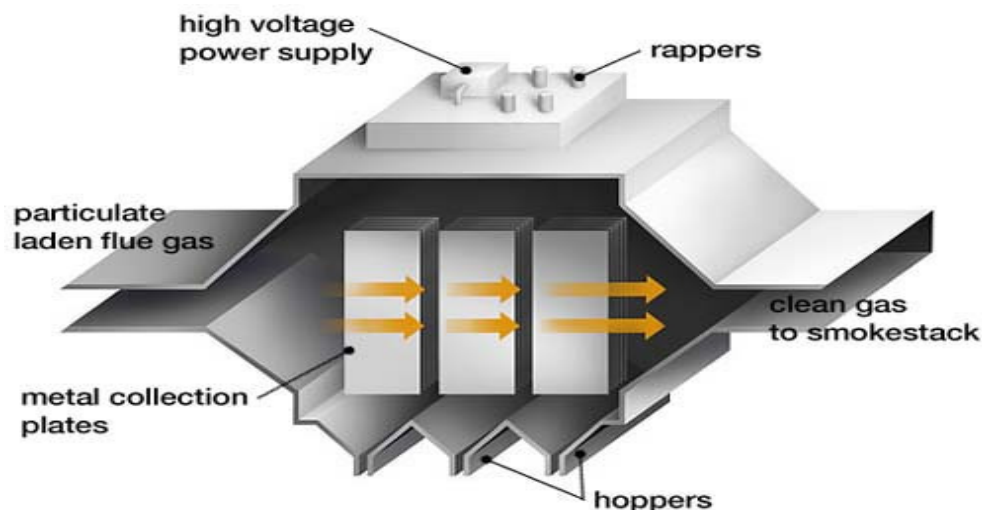

Figure 0-1: A schematic overview of an electrostatic precipitator[4]

The foreseen location of this device in a post combustion capture plant would be behind the washing section. This would lead to a substantial enlargement of the needed footprint.

It is of importance to note that an ESP will lower the aerosol based emission. Amines and ammonia present as vapour will not be removed from the gas phase.

1.4.1 Additional CAPEX

For a gas-fired installation the expected CAPEX would be 30 to 40 keuro/MW installed (conservative estimate). This would be for the 430 MW case between 13 and 17 million euro.

In Figure 2.2 the unit capital cost is given for an ESP. The data is from 2002 and for oil fired power plants (ref *Reference Costs and Parameters for Project formulation in the electric sector 2002.*

---

[4] SO2, NOx, and Particle Control Technologies and Abatement Costs for the Mexican Electricity Sector by Jorge Islas S., Fabio Manzini P., Genice Grande A., María Pérez O. (Centre for Energy Research (CIE), UNAM, México), 2005

Generation. COPAR 2002. (in Spanish). Gerencia de Evaluación y Programación de Inversiones, Comisión Federal de Electricidad)
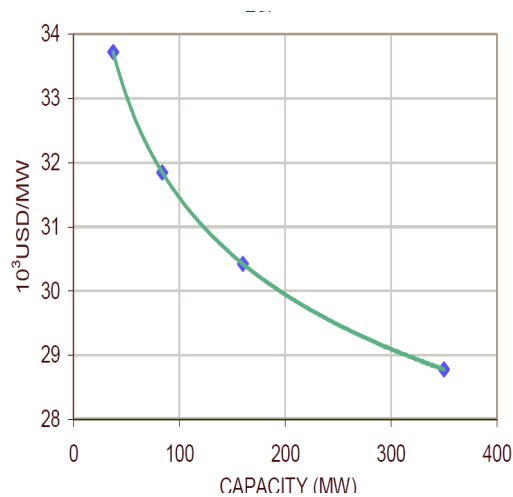

Figure 2.2 Unit capital cost for an ESP.

1.4.2 Additional OPEX

An estimation of the operational expenditure of the ESP (ie unit operation and maintenance cost) is around 1 to 2 euro's per MWh. This would entail for the 430 MW case, an additional cost of 1.6 to 3.2 million euro per year. Per ton of CO_2 captured this would be in the neighbourhood of 1.5 to 3 euro's.

In Figure 2.3 the operational is given for an ESP. The data is from 2002 and for oil fired power plants (ref *Reference Costs and Parameters for Project formulation in the electric sector 2002*. Generation. COPAR 2002. (in Spanish). Gerencia de Evaluación y Programación de Inversiones, Comisión Federal de Electricidad).

PROJECT NO.
801862

REPORT NO.
F21929

VERSION
2

10 of 44
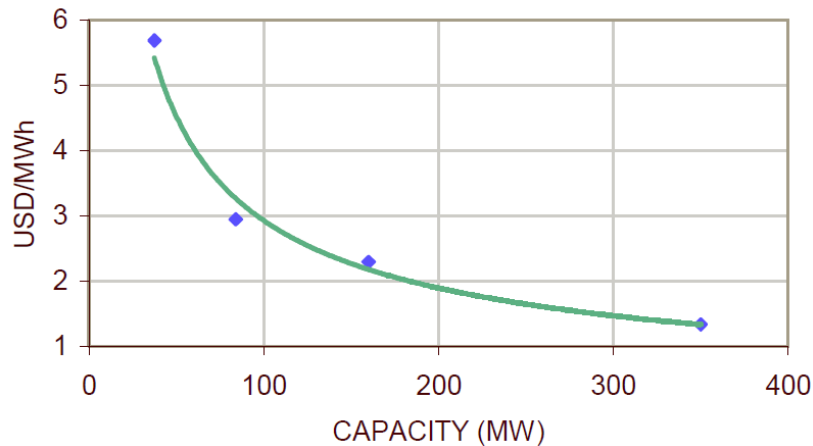
Figure 0-3: Operational costs for an ESP

1.4.3 Preliminary conclusion and open research questions

(Wet) electrostatic precipitators would most likely be usable for the reduction of aerosols in the size range above 1 micrometer. In principal electrostatic precipitators can be used in the appropriate scale. From a CAPEX and OPEX point of view, this would be a rather cost intensive option. There is a substantial level of information available dealing with large scale operation of electrostatic precipitators for the reduction of small particles. However, there is no experience with reducing aerosols formed from post combustion capture processes by electrostatic precipitators. Research questions are:

- Efficiency
- Power consumption
- Waste handling
- Technical lifetime

Regarding HSE, waste disposal is an important topic. However, the generated amount of liquid would be relatively small. This needs further investigation.

1.5 UV-treatment

As mentioned in the appendices UV-treatment could be an option to lower the amount of nitrosamine in the absorption liquid, wash liquid and the subsequent treated flue gas. Proof of principle has been established using smaller versions of capture plants. From the initial proof of principle experiments, can be concluded that the most suitable position of an UV-treatment system is in the washing liquid and stripper condensate.

The amount of energy needed and size of the equipment is depended on the desired levels of nitrosamine. In a next phase, this could be more substantiated. Nevertheless, UV-treatment is a

technology which can be scaled to the appropriate sizes (see Figure 2-4 for an example from the potable water industry).

Figure 0-4: UV-treatment of potable water

Concluding, it can be stated that UV-treatment is possible, (particularly for treatment of the wash and condensate liquids). However, preliminary results indicate that the efficiency of UV-treatment directly in the absorption liquid is limited. Moreover, at this moment not enough data is available to make quantitative estimates for CAPEX and OPEX. Therefore, the recommendation is to limit the research activities in this field. Nevertheless, it would be beneficial to have a technology available which can be used to reduce the nitrosamine level in the absorption liquid. Based on preliminary research done at TNO and at SINTEF, adsorption and hydrogenation could be such a technique (see below and Appendices).

From an HSE point of view, it is of importance to note that attention should be placed on working conditions with strong UV light sources.

1.6 Alternative reduction technologies: Hydrogenation and Adsorption

It has been reported that nitrosamine can be reduced with hydrogen and a Nickel catalyst. The results suggest that this is a viable option for nitrosamine destruction. Such a catalyst can be an option both in the process (in the solvent loop) and in the water-wash unit. Preliminary experiments have already been executed (see Appendix) and showing good results of the reduction of nitrosamine in an amine based matrix. Therefore, one of the recommendation would be to use a relatively small budget to do scouting research on this topic. This scouting research should lead to a proof of principle and a first technical and economic evaluation.

Next to hydrogenation, adsorption looks also as an interesting option (see Appendix). It has been reported that several materials are capable of adsorbing nitrosamines. However, the main challenge would be in the identification of suitable adsorption materials which can be used in a complex mixture like the absorption liquid. A recommendation would be to do scouting research on this topic to investigate the potential of this separation technique.

Envisaged work plan

This chapter is focussed on the items which can be further researched in a next phase. The items listed below are based on the lessons learned during this project. In the appendices more information can be found on the rationale for the outline of the next phase. In general, it can be stated that this work is directed towards the demonstration of scalable and cost efficient emission countermeasures focused on aerosol and nitrosamine/amine reduction.

Item list	Main objective	Type of activity	Rough cost estimate (k€), without risk and project management
Item 0: Understanding aerosol formation and develop guidelines for running absorption plants	Establish quantitative relationship between key process factors and aerosol emission	Modelling Pilot plant investigation	205
Item 1: Scouting research	Develop proof of principle for two nitrosamine removal techniques: hydrogenation and adsorption	Laboratory investigation	110
Item 2: Proof of principle of an electro static precipitator	Detailed investigation on the usability and the technical/economic details of an electrostatic precipitator Preparation for ITEM 4A	Desk study	120
Item 3: Proof of principle acid wash	Detailed investigation on the usability and the technical/economic details of an acid wash step Preparation for ITEM 4B	Modelling	170
Item 4a: Demonstration (proof of concept) electrostatic precipitator	Proof of concept electrostatic precipitator Determine scale up parameters	Pilot plant demonstration	380
Item 4B: Demonstration (proof of concept) acid wash unit	Proof of concept acid wash unit Determine scale up parameters	Pilot plant demonstration	310

Based on the results from Item 2 and Item 3, go/no go decision can be made for Item 4A/B.

The above mentioned items can be further worked out in a work plan upon request.

Item 0: Understanding of aerosol formation

Objective:

- Determine quantitative relationship between aerosol formation and operating conditions and flue gas quality.

Approach:

Operation of the Maasvlakte pilot plant under gas fired conditions with and without the Brownian Demister Unit **before** the absorber. Pilot plant will be operated with different capture ratio to investigate the influence of the temperature profile within the absorber on the aerosol formation

Activities:

The following activities need to be done:

- Adjustment hardware: BDU in front of the absorber
- Online gas phase measurements using FT-IR before and after wash section
- Offline gas phase measurement by impinger methodology
- Aerosol measurements by APS and ELPI inlet gas, before water wash and after wash

Duration:

The experimental campaign could be finished within two weeks. Aging of the solvent (30wt% MEA) is not needed. TNO will operate the pilot plant. SINTEF will do offline gas phase measurements and modelling.

After this task, the following items are known:
- Influence of inlet gas quality on aerosol formation
- Influence temperature profile on aerosol formation
- Origin distribution aerosol absorber and wash section

Item 1: Scouting research

Objective:

- Research the potential of hydrogenation and adsorption for the removal/destruction of nitrosamine[5]

Approach:

Laboratory investigation of the potential of two different NA removal techniques. Based on the results a technical and economic evaluation will be made for the reference case

Activities:

The following activities need to be done:

- selection of appropriate hydrogenation catalyst
- batch wise testing hydrogenation for different matrices (absorber liquid, wash liquid, condensate). Main criteria are selectivity, activity and stability of the catalyst.
- proof of principle[6] hydrogenation absorber liquid using a continuous absorber/desorber equipment using artificial flue gas
- Technical and economic evaluation of hydrogenation for the reference case
- selection of appropriate adsorbtion material
- batch wise testing adsorbentia for different matrices (absorber liquid, wash liquid, condensate). Main criteria are selectivity and stability of the adsorbens.
- proof of principle[7] adsorbentia absorber liquid using a continuous absorber/desorber equipment using artificial flue gas

Duration:

These activities are predominantly lab based. They can be performed at TNO or SINTEF. Typically, this more explorative research will have an approximate duration of 3 months.

After this task, the following items are known:
- The optimal location for hydrogenation (eg side stream wash liquid/absorption liquid)
- The potential of removal of nitrosamine by hydrogenation based on a technical and economic evaluation

- The optimal location for adsorption (eg side stream wash liquid/absorption liquid)
- The potential of removal of nitrosamine by adsorption based on a technical and economic evaluation

---

[5] These techniques are proposed based on discussions and preliminary research done at SINTEF and at TNO
[6] Only in case that batch wise hydrogenation demonstrated a good potential for the direct treatment of the absorption liquid (eg. selectivity and activity)
[7] Only in case that batch wise adsorption test demonstrated a good potential for the direct treatment of the absorption liquid (eg. selectivity and stability)

Item 2: Proof of principle electrostatic precipitator

Objective

- Technical and economic evaluation (+/- 50%) for a reference case
- Develop test plan proof of concept
- Design proof of concept (ie connected with a pilot plant)

Approach:

Inventarisation (incl. discussion with vendors and users of electrostatic precipitors) of usable ESP units. Preparation for the proof of concept at the pilot plant. Based on the results, a go- no go decision can be made for item 4A.

Activities:

The following activities are needed:

-   inventarisation technical possibilities ESP incl. technical and economic evaluation (CAPEX and OPEX)
-   develop test plan
-   select appropriate ESP unit for the pilot plant
-   detailed cost estimation for ITEM 4A

Timings:

This activity could be done within 2 months.

After this task, the following items are known:
-   Cost estimate for an electrostatic precipitator for a given reference case
-   Test plan for demonstrating electrostatic precipitator at the Maasvlakte pilot plant
-   Detailed cost estimation Proof of Concept (item 4A)

Item 3: Proof of principle acid wash

Objective

- Determine scaling up parameters (experimental and modelling)
- Technical and economic evaluation (+/- 50%)
- Develop test plan proof of concept
- Design proof of concept (ie connected with a pilot plant)

Approach:

Rate based modelling tool will be developed, which can be used to design an acid wash unit. Based on this, a technical and economic evaluation will be made for such a unit. Next to that, the preparation for the proof of concept at the pilot plant will be done. Based on these preparations, a go- no go decision can be made for item 4B.

Activities:

The following activities are needed:

- Rate based modelling tool
- Technical and economic evaluation
- develop test plan
- design acid wash unit for the pilot plant
- detailed cost estimation for ITEM 4B

Timings:

This activity could be done within 3 months.

> After this task, the following items are known:
> - Cost estimate for an acid wash unit for a given reference case
> - Test plan for demonstrating acid wash unit at the Maasvlakte pilot plant
> - Detailed cost estimation Proof of Concept (item 4B)

Item 4A: Proof of Concept Electrostatic Precipitator

Objective:

- Proof of concept (ie connected with a pilot plant)
- Technical and economic evaluation of (W)ESP (+/- 50%[8])

Approach:

Demonstration of an electrostatic precipitator at the Maasvlakte pilot plant. Rigorous analytics (on- and offline) to understand the potential of an ESP in a post combustion capture process. Based on the performance, a scale-up study will be made. This study will be used for a technical and economic evaluation (CAPEX and OPEX).

Activities:

The following activities are needed:

- Build test setup
- Acceptance tests ESP
- Trial ESP according to test plan
    - Analysis will be done using FT-IR (in- and outlet stream)
    - Impinger tests
- Pragmatic model based on the experimental results
- Scale-up study, technical and economic evaluation

Duration:

The total activities could be performed within 6 months. Trial campaign would be in the order of four weeks.

After this task, the following items are known:
- The potential of electrostatic precipitator to reduce aerosol emissions
- The technical and economic evaluation of an electrostatic precipitator

---

[8] A suitable case with User Requirements should be made available

Item 4B: Proof of Concept Acid wash

Objective:

- Proof of concept (ie connected with a pilot plant)

- Technical and economic evaluation of additional acid wash step (+/- 50%[9])

Approach:

Demonstration of an additional acid wash at the Maasvlakte pilot plant. Rigorous analytics (on- and offline) to understand the potential of an acid wash step in a post combustion capture process. Based on the performance, a scale-up study will be made. This study will be used for a technical and economic evaluation

Activities:

The following activities are needed:

- develop test plan

- select acid wash equipment and build setup

- Acceptance tests acid wash unit

- Trial acid wash unit according to test plan

  o Analysis will be done using FT-IR (in- and outlet stream)

  o Impinger tests

- Thermodynamic model based on the experimental results

- Scale-up study[10], technical and economic evaluation (CAPEX and OPEX)

Duration:
The total activities could be performed within 6 months. Trial campaign would be in the order of four weeks.

> After this task, the following items are known:
> - The potential of an acid wash to reduce MEA (from the vapour phase) and ammonia emissions
> - The technical and economic evaluation of an acid wash unit

---

[9] A suitable case with User Requirements should be made available
[10] Waste handling would be part of this work-package

Summary and conclusions

This report describes the preliminary work focused at the reduction of emissions from post combustion capture plants. An assessment is made dealing with the available technologies. Two technologies, acid wash and electrostatic precipitator, have been examined in more detail. The main advantage for the acid wash technology is that low emissions of amines and ammonia present in the vapour phase can be obtained. The impact of an acid wash step on aerosols should be further investigated. However, research done in other projects suggests that an acid wash system can have an impact on aerosol based emission of MEA. The main advantage of an electrostatic filter is that a high reduction of aerosols can be obtained. A drawback is the relatively high capital expenditure. It seems that upon combining both systems a very environmentally friendly capture plant can be designed.

Recommendations have been made for future work. These recommendations are based on:

- understanding aerosol based emission by dedicated pilot plant activities.
- scouting research to two promising techniques for the removal of nitrosamine from the capture solvent by hydrogenation and adsorption
- development and pilot plant testing of electrostatic precipitators and additional acid wash scrubbers to lower the emissions from post combustion capture plants

These recommendations should lead to large scale implementable techniques for the reduction of aerosols and vapour based emissions of in particular amines, nitrosamines and ammonia.

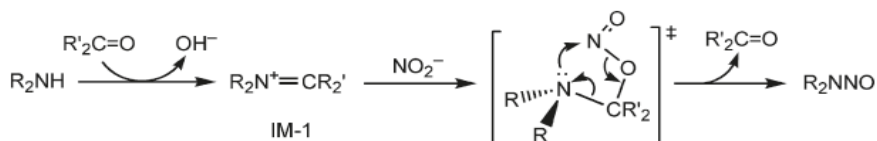## Appendix 1: Nitrosamine formation

Nitrosamine formation: chemistry

Although the exact reaction mechanism is not clear there are some indications that the presence of CO2 can be an catalyst for the formation of nitrosamine. In Figure A-1, reaction mechanism towards the formation of NDMA is given, for different nitrosating agents.
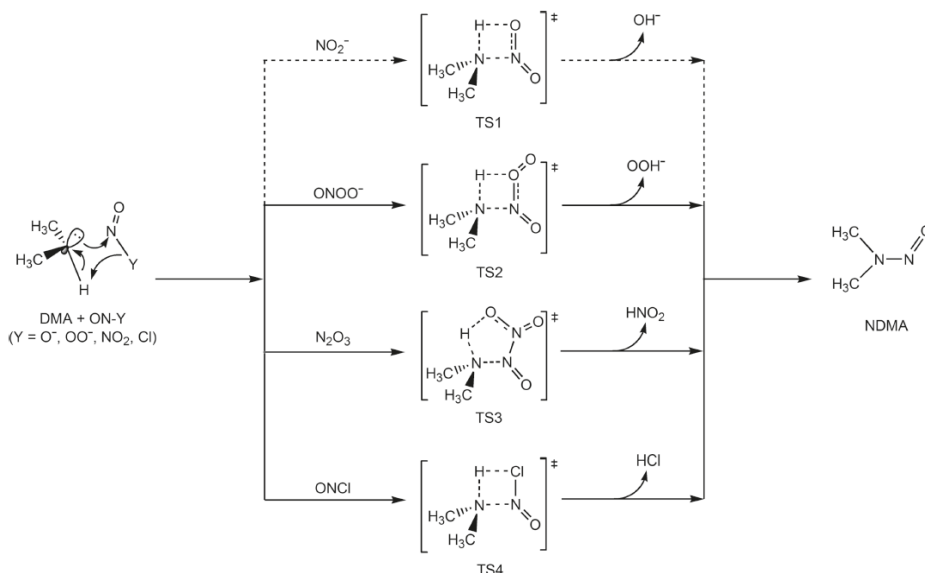

Figure A-1: reaction pathways for the formation of NDMA for different nitrosating agents

It is known that some impurities can lead to a faster formation rate of nitrosamine. In Figure A-2, a tentative scheme is given for the influence of aldehydes on the reaction mechanism. It is of importance to note that aldehydes are frequent degradation product present in the absorption liquid (e.g. formaldehyde).

Figure A-2: reaction mechanism using aldehydes as catalyst

It has been hypothesized that CO_2 can also be a catalyst for the formation of nitrosamine. For a tentative scheme, see Figure A-3.
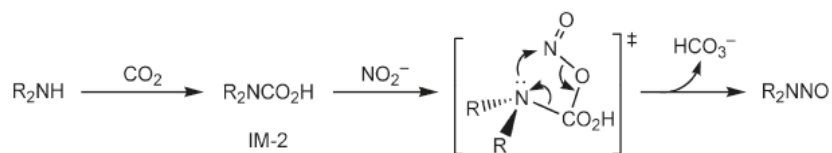
Figure A-3: CO_2 as catalyst for the formation of nitrosamine

For an MEA based system the typical expected nitrosamines are:
- NDMA
- NDELA
- N-morpholine (N-MOR)

In the sections below, the likeliness of formation NDMA and N-MOR are discussed.

NDMA

Physical properties NDMA[11]

N-Nitrosodimethylamine, or NDMA, is the simplest dialkylnitrosamine, with a molecular formula of $C_2H_6N_2O$ and a relative molecular mass of 74,08 (ATSDR, 1989) (Figure A-4). NDMA belongs to a class of chemicals known as *N*-nitroso compounds, characterized by the *N*-nitroso functional group (–N–N=O), and to the family of nitrosamines, which, in addition, possess an amine function (–NR$_2$, where R is H or an alkyl group). NDMA is also known as dimethylnitrosamine, dimethylnitrosoamine, *N,N*-dimethylnitrosamine, *N*-methyl-*N*-nitrosomethanamine, *N*-nitroso-*N,N*-dimethylamine, DMN, and DMNA. NDMA has the Chemical Abstracts Service (CAS) registry number 62-75-9.
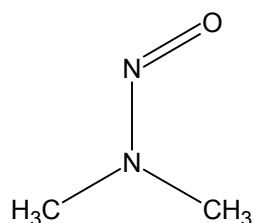
Figure A-4: Chemical structure of NDMA.

[11]) N-Nitrosodimethylamine, Concise International Chemical Assessment Document 38, First draft prepared by R.G. Liteplo and M.E. Meek, Health Canada, Ottawa, Canada, and W. Windle, Environment Canada, Ottawa, Canada, World Health Organization, Geneva, 2002

NDMA is a volatile, combustible, yellow, oily liquid. It is susceptible to photolytic breakdown due to its absorption of ultraviolet light. The physical/chemical properties relevant to the emission of NDMA are presented in Table A-1.

Table A-1: Physical and chemical properties of NDMA.

Physical/chemical property	Value
Melting point (°C)	50
Boiling point (°C)	151–154
Log K_{ow}	0,57
Vapour pressure	1080 Pa (25 °C)
Henry's law constant	3,34 Pa m^3/mol (25 °C)
Solubility	Miscible

Miscellaneous: The conversion factor for NDMA in air is 1 ppm = 3,08 mg/m^3.

Reaction mechanism formation NDMA

NDMA is most likely formed via the reaction of nitrite with dimethylamine. The exact reaction mechanism for this reaction is not entirely known. Most likely the reaction is catalysed by the presence of aldehydes, such as formaldehyde. The origin of dimethylamine (DMA) is most likely due to oxidative degradation with diethanolamine (DEA). DEA can be already present in the MEA as impurity. Next to that also DEA can be formed by deamination of MEA (see Figure A-5).
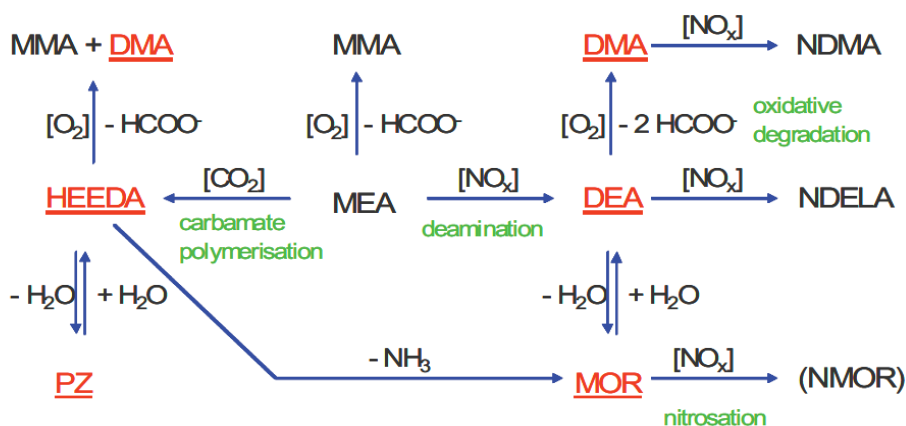
Figure A-5: Tentative reaction pathway for the formation of NDMA [12]

Likelihood of formation of NDMA

As stated above for the formation of NDMA, the presence of dimethylamine is required. Dimethylamine is a very volatile component. The vapour pressure at 20°C is 1.7 bar. This means that if dimethylamine is formed during post combustion capture of CO_2, this will be emitted directly in the absorber or in the stripper. DMA will not be captured in the first washing stage and returned to the absorber by the return of the condensed water. Therefore, the presence of DMA will be very limited. This, therefore, means that it is not very likely that NDMA will be present to a large extent.

From laboratory experiments[12], it is known that NDMA can be formed under realistic conditions. However, the level is very low compared to the formation of other less volatile nitrosamines. This confirms the above mentioned statement that it is not very likely that NDMA will be the major nitrosamine constituent. It is more likely that Nitrosodiethanolamine will be the major nitrosamine constituent.

N-MOR

Properties of N-MOR

In Figure A-6, the molecular structure of N-MOR is depicted.
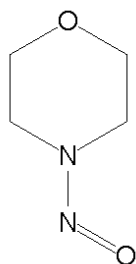
Figure A-6: Chemical structure of N-MOR

In Table A-2 below an overview can be found of some of the relevant properties of N-MOR.

Table A-2: Physical properties of N-MOR (GSI CHEMICAL PROPERTIES DATABASE)

| Nitrosomorpholine, N-	CAS No. 59892
Physical Properties	**Value**
Molecular Weight (g/mol)	116,1194
Solubility @ 20-25 degC (mg/L)	4713864,008
Vapor pressure @ 20-25 degC (mmHG)	0,02964944361
Henry's Law constant @ 20 degC	3,9949441671e-008
Sorption coefficient (log L/kg) Koc	-1,3652121682
Octanol-water partition coefficient (log L/kg)	-1,389106987
Diffusion coefficient in air (cm^2/s)	0,07413870474
Diffusion coefficient in water (cm^2/s)	9,2160606782e-006

---

[12] Effects of NOx in the flue gas degradation of MEA
Berit Fostås, Audun Gangstad, Bjarne Nenseter, Steinar Pedersen, Merethe Sjøvoll and Anne Lise Sørensen, Energy Procedia, Volume 4, 2011, Pages 1566-1573

It is of importance to note that N-MOR has an ability to induce cancer. However, compared with NDMA, N-MOR has a lower potency.[13]

Formation route N-MOR

N-MOR can be formed based on the reaction of nitrite with morpholine (MOR). MOR is a secondary degradation product from MEA. The secondary degradation product MOR originates to a great extent from the degradation products N-(2-hydroxyethyl)-ethylenediamine and diethanol-amine (see Figure A-7).
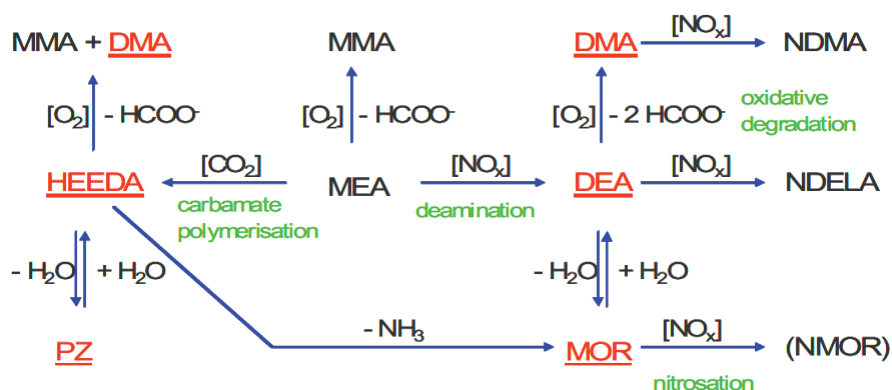
Figure A-7: Tentative formation route for N-MOR[12]

In other pilot plant operations (CESAR campaign), N-MOR has been detected, but only in sub ppb level.[14] The results presented in [15] indicate that N-MOR has not been detected in liquid samples, but only as a trace compound in autoclave gas samples.

Conclusions for the assessment of emissions

N-MOR can be formed during post combustion capture of CO_2. However, compared with NDELA and for the reasons stated above, this would be a minor component. It is of importance to note that the volatility and the wash efficiency of N-MOR is between NDMA and NDELA. Therefore, if N-MOR will be

---

[13] Health effects of amines and derivatives associated with CO_2 capture
Marit Låg, Birgitte Lindeman, Christine Instanes, Gunnar Brunborg and Per Schwarze; Published by The Norwegian Institute of Public Health, Division of Environmental Medicine, Department of Air Pollution and Noise, Department of Chemical Toxicology, April 2011

[14] Emission measurements at Dong's pilot plant for CO_2 capture in Esbjerg, da Silva, E. F. and Aas, N (2010), work done in the EU project Cesar, presented at IEA Greenhouse Gas R&D Programmes workshop on Environmental Impact of Amine Emission During Post Combustion Capture, Oslo, Norway.

[15] Effects of NOx in the flue gas degradation of MEA
Berit Fostås, Audun Gangstad, Bjarne Nenseter, Steinar Pedersen, Merethe Sjøvoll and Anne Lise Sørensen, Energy Procedia, Volume 4, 2011, Pages 1566-1573

present in the absorption liquid, washing will lead to a strong reduction of any N-MOR present in the treated flue gas. Moreover, the toxicity of N-MOR (potency) is lower compared with components such as NDMA. This leads to the conclusion that the impact of N-MOR on the overall emissions is low.

Appendix 3: Aerosol formation

As can be found in the Appendixes 3 and 5, aerosol formation can occur due to:

- Mechanical entrainment
- Aerosols formed by reactions
- Aerosols formed by condensation

If importance to note is that mechanical entrainment is dependent on the operating conditions and the solvent quality (e.g. surface tension). Surface tension for instance is dependent amongst others on the degradation of the amine. Typically, droplets formed by mechanical entrainment are larger then formed by the two other mechanisms.

Aerosol formed by reaction, is not something what would be occurring to a significant degree in natural gas fired power-plants. The reason for this is that the level of acidic components (e.g. SO_2) would be quite low.

Aerosol formed by condensation, is something what could occur in gas fired power-plants. Crucial for this, is the temperature profile and the presence of heterogeneous condensation nuclei. Typically, this would have a stronger impact for coal fired power plants. However, in the case of gas fired power-plants relatively more flue gas per MW will pass through the absorber.

Options to lower aerosol formation are:

- Creating a more gently temperature profile in the absorber (e.g. lower net capacity of the solvent, intercooling)
- Reducing nuclei in the to be treated flue gas (e.g. reduction of particulate matter)

SINTEF

Appendix 3: MEMO SINTEF 2011-11-25

Memo
Emission reducing Technologies

PERSON RESPONSIBLE / AUTHOR Eirik Falck da Silva, Kamal Nazrague and Earl Goetheer (TNO)	FOR YOUR ATTENTION	COMMENTS ARE INVITED	FOR YOUR INFORMATION	AS AGREED
DISTRIBUTION		X		X
CCM				

PROJECT NO / FILE CODE	DATE	CLASSIFICATION
801862	2011-11-25	Confidential

The present memo is intended to summarise emission reducing technologies that may be implemented in amine based CO_2 capture plants.

In the present memo it is assumed that the emissions one wishes to control are of the solvent itself, nitrosamines and nitramines.

The plant emissions can be separated into two contributions:
1. Gas phase emission
2. Aerosol and droplet emissions

Emission reducing technologies can be separated according to the principle they are based:
1. Limiting gas phase emissions
2. Limiting aerosol emissions
3. Destruction of compounds in the emission
4. Limiting the formation of nitrosamines and nitramines

In Table C-1 emission reducing technologies and concepts are listed. In the table we have grouped together all removal techniques specific to nitrosamines and nitramines.

Table C-1: Emission reducing technologies

Class of ERT	Nitrosamine/nitramine specific removal	Gas emission control	Aerosol emission control	Organic compound removal
	E: UV in water-wash	E: Water-wash	E: Brownian diffusion demistors	C: Electrochemical destruction in water-wash
	E: NOx scavenger in water-wash	E: Acid-wash	E: Wet electrostatic precipitator	C: Advanced oxidation in water-wash
	C: Nitrite oxidation or scavenger in process	C: Adsorption on solids	E: Cold plasma technology	C: Adsorption of solids in water-wash (for example zeolites)
	C: Catalytic hydrogenation of nitrosamines in process		C: Removal of condensation nuclei from exhaust gas stream	
	C: Radical scavengers in process to control nitrosamine formation		C: Electrostatic precipitator	
	C: Catalytic hydrogenation of nitrosamines in water-wash		C: Control of temperature gradients in absorber column	
	C: Removal of NOx from exhaust gas before absorber			

E: Indicates a specific emission reducing technology
C: Indicates a potential concept for a emission reducing technology
Technologies marked in green are recommended for further study in the present project.

In Table C-1 we have distinguished between emission reducing technologies "E" and concepts "C". The concepts are ideas for emission control, but where we do not have enough information at present to design a capture unit based on this concept.

A challenge for the present assessment is that we are not aware of industries or technology applications with the same emission issue. There is therefore limited data that is directly applicable to CO_2 capture processes.

General comment
Residence times are a key limitation for implementation of emission reducing technologies. Another key factor is energy consumption.

PROJECT NO.
801862

REPORT NO.
F21929

VERSION
2

29 of 44

Options not considered

Biological removal techniques are likely to require to long residence times to be used in main units of emission control.

Quantitative understanding

There is at present little published data relevant to the assessment of ERT technologies for CO_2 capture plants. We do however have a different degree of understanding of how different emission reducing technologies will work. In Table C-2 we have attempted to indicate for which technologies/concepts we have a reasonable understanding of the performance of such a technology. Quantitative understanding indicates a high enough level of understanding to design a capture unit based on the technology.

Table C-2: Quantitative understanding of Emission reducing technologies

Class of ERT	Nitrosamine/nitramine specific removal	Gas emission control	Aerosol emission control	Organic compound removal
	E: UV in water-wash	E: Water-wash	E: Brownian diffusion demistors	C: Electrochemical destruction in water-wash
	E: NOx scavenger in water-wash	E: Acid-wash	E: Wet electrostatic precipitator	C: Advanced oxidation in water-wash
	C: Nitrite oxidation or scavenger in process	C: Adsorption on solids	E: Cold plasma technology	C: Adsorption on solids in water-wash (for example zeolites)
	C: Catalytic hydrogenation of nitrosamines in process		C: Removal of condensation nuclei from exhaust gas stream	
	C: Radical scavengers in solvent to control nitrosamine formation		C: Electrostatic precipitator	
	C: Catalytic hydrogenation of nitrosamines in water-wash		C: Control of temperature gradients in absorber column	
	C: Removal of NOx from exhaust gas before absorber			

Green indicates a technology for which we have a reasonable understanding of capture efficiency.

The effect of water-wash units is generally well understood, although significant work may remain in finding their optimal design. The principles of acid wash are also well understood although their efficiency in CO_2 capture plants has not been demonstrated in open literature.

It is also known that nitrosamines degrade readily in UV light. It therefore seems very likely that UV-light will be efficient in destroying nitrosamines in the water-wash unit. While we are that different

PROJECT NO.
801862

REPORT NO.
F21929

VERSION
2

30 of 44

organizations have initiated studies of utilization of UV light to control emissions from CO_2 capture plant, we are not aware of any published data demonstrating effect on emissions.

NOx scavengers could be added in the water-wash to prevent formation/reformation of nitrosamines and nitramines. While we are not aware of any relevant studies on this technology, it does seem to be a feasible option.

Wet electrostatic precipitators (WESP) do seem to be entirely viable emission reducing technology for CO_2 capture plants. At present we do not, however, have a model to say what WESP unit design is suitable for a CO_2 capture plant.

For the other technologies and concepts we do not relevant data to judge what type of design (if any) would make it a suitable emission reducing technology for CO_2 capture plants. These would need to be studied further before one could propose implementation at a CO_2 capture plant.

Recommended technologies

The technologies recommended for further study are:
Advanced water-wash

- 2 or 3 stages, with possibility for UV treatment of wash-water.

- Should have possibility for acid wash in one stage and addition of NOx scavenger.

- Options should be explored to maximize addition of make-up water in the water-wash unit.

- Should also look at options to control the degree of cooling in different water-wash stages.

Wet-electrostatic precipitator
This would seem to be robust technology for removal of aeorosols. It would be installed after the water-wash unit of the plant.

Comments on specific technologies

Frierdich et al. (2008) report on reduction of nitrosamines with Hydrogen and a porous Nickel catalyst. The results suggest that this is a viable option for nitrosamine destruction. Such a catalyst can be an option both in the process (in the solvent loop) and in the water-wash unit.

Cao et al. (2007) report a method adsorbing a nitrosamine in zeolites. The experiments here are however quite different from conditions in CO_2 capture plant. It is therefore very difficult to draw conclusions on whether such a material could be used for efficient removal in a CO_2 capture plant.

The use of nanosponge cyclodextrin polyurethanes for the removal of nitrosamines from water has also been reported (Mhlongo et al. 2009 and references therein).

Landsman et al. (2007) report on advanced oxidation methods for removal of nitrosamines. Such technology is clearly an option in the water-wash system. In the solvent loop advanced oxidation methods could potentially destroy solvent components.

Rondlöf et al. (2000) report work on nitrite scavengers to inhibit the formation of nitrosamines. Ascorbic acid is mentioned as an efficient inhibitor. Wang et al (2005) report on sulfamic acid as a nitrite scavenger. Such scavengers may be utilized in the water-wash unit of a CO_2 capture plant. We are however not aware of any such scavenger or inhibitor that is reported to work at the basic conditions encountered in the amine solvent. It is at present difficult to draw any conclusions as to whether nitrite scavengers are a feasible option in the solvent loop.

There are several options for removal of NOx from the exhaust gas. A well established technology is selective catalytic reduction with ammonia. Hitachi have reported 90% NOx removal with such technology (Morita et al. 2002), and even greater removal may perhaps be achieved.

A novel technology for the removal of NOx and SOx is electron beam flue gas treatment (EBFGT) (Edinger 2008 and Chmielewski et al. 2002). Such a concept does however require an electrostatic precipitator.

Removal of NOx from the flue gas is in a sense a very simple and attractive option. Limiting the NOx uptake in the plant may be enough to limit the nitrosamine build-up in the plant to acceptable levels. The gas-fired power plant at Mongstad has low NOx emissions and reduction to very low levels may be achievable.

(Dry) Electrostatic precipitators are a technology for removing aerosols based on the charging of particles. While wet-electrostatic precipitators seems to be the most established for use at power plants, other precipitators could also be considered.

Potential further work for other technologies
In Table C-3 and Table C-4 we have listed recommended activities for the further development of other emission reducing technologies and concepts. Table C-3 contains the technologies that in our judgement seem the most promising.

In general it can be noted that there are a number of options for controlling the concentration of nitrosamines and nitramines in the water-wash.

There does however appear to be more limited options for removing components from the gas phase or aerosols.

For limiting gas-phase emissions water-wash based systems would seem to be the most attractive option. Another option is oxidizing or in other way reacting or destroying components in the gas phase, but for some of these processes needed reaction time is likely to be an issue. Electron beam flue gas treatment (EBFGT) may be an interesting option.

For limiting aerosol emissions there does appear to be a limited number of capture concepts. The concepts we are see are either based on filtration or electrostatic interactions. Aerosol emissions do also at present appear to be the potentially greatest challenge in controlling emissions from post-

PROJECT NO.
801862

REPORT NO.
F21929

VERSION
2

32 of 44

combustion CO_2 capture plants. The greatest attention should therefore go towards looking at technologies for efficient control of aerosol emissions.

Table C-3: Recommended work for other promising Emission reducing technologies

ERT	Recommended next step of development
C: Catalytic hydrogenation of nitrosamines in process	1. Review of catalysts and design for process 2. Testing on synthetic solvent or small pilot unit
C: Nitrite oxidation or scavenger in process	1. Review of potential scavengers and processes for oxidation. 2. Testing on synthetic solvent or small pilot unit
C: Catalytic hydrogenation of nitrosamines in water-wash	1. Review of catalysts and design for process 2. Testing on synthetic wash-water or small pilot unit
C: Radical scavengers in process to control nitrosamine formation	1. Review of suitable scavengers 2. Testing on synthetic solvent or small pilot unit
C: Removal of condensation nuclei from exhaust gas stream	1. Review of removal concepts 2. Testing on pilot plant with relevant gas stream
C: Electrostatic scrubber	1. Review of commercially available technologies. 2. Testing on pilot plant with relevant gas stream
C: Control of temperature gradients in absorber column	Study of temperature gradients on emission profile in one or more pilot plant.
C: Removal of NOx from exhaust gas before absorber	1. Review of commercially available technologies. 2. Testing on pilot plant with relevant gas stream. The testing could focus on extent of nitrosamine uptake in the plant. Measuring the effect on nitrosamine emissions may require a very long campaign.

Table C-4: Recommended work for less promising Emission reducing technologies

ERT	Recommended next step of development
C: Electrochemical destruction in water-wash	1. Testing of concept in lab scale apparatus with synthetic water-wash 2. Testing in small pilot plant
C: Advanced oxidation in water-wash	1. Review of design options 2. Testing in lab scale apparatus 3. Testing in small pilot plant
C: Adsorption of solids in water-wash (for example zeolites)	1. Review of potential materials 2. Testing of concept in lab scale apparatus with synthetic water-wash 3. Testing in small pilot plant
C: Adsorption on solids (to capture compounds from the gas phase emissions)	1. Review of suitable materials 2. Testing in lab-setup or small pilot unit
E: Cold plasma technology	1. Obtain data from vendors or technology developers. 2. Testing in small pilot unit.

Conclusion

An advanced water-wash system is recommended as a technology for further study. Such an advanced water-wash may integrate UV treatment of water and the use of acid-wash and NOx scavengers.

Another technology that is recommended for further study is wet-electrostatic precipitators.

There are also a number of other technologies and concepts that can be explored for use in emission control. For these we do however at present not have enough knowledge to design a unit for implementation at a CO_2 capture pilot plant.

References

Cao, Y. et al (2007) Removal of carcinogens in environment: Adsorption and degradation of N0-nitrosonornicotine (NNN) in zeolites. *Microporous and Mesoporous Materials* 103, 352–362.

Chmielewski, A. G., Sun, Y., Zimek, Z., Bulka, S. and Licki, J. (2002). Mechanism of NOx removal by electron beam process in the presence of scavengers. Radiation Physics and Chemistry 65, 397–403.

Edinger, R. (2008), Reduction of SOx and NOx emissions by electron beam flue gas treatment

Frierdich, A. J., Shapley, J. R. and Strahtmann, T. J. (2008) Rapid Reduction of N-Nitrosamine Disinfection Byproducts in Water with Hydrogen and Porous Nickel Catalysts. *Environ. Sci. Technol.* 42, 262–269.

Landsman, N. A. (2007) Free Radical Chemistry of Advanced Oxidation Process Removal of Nitrosamines in Water. *Environ. Sci. Technol.* 41, 5818-5823.

Mhlongo, S. H., Mamba, B. B. and Krause, R. W. (2009) Nitrosamines: A review on their prevalence as emerging pollutants and potential remediation options. Water SA Vol. 35 No. 5.

PROJECT NO.
801862

REPORT NO.
F21929

VERSION
2

34 of 44

Morita, I., Ogasahara, T. and Franklin, H. N. (2002) recent experience with hitachi plate type scr catalyst. The Institute of Clean Air Companies Forum '02.

Rundlöf, T. et al (2000) Potential Nitrite Scavengers as Inhibitors of the Formation of N-Nitrosamines in Solution and Tobacco Matrix Systems. *J. Agric. Food Chem.* 48, 4381-4388.

Appendix 5: MEMO TNO Nitrosamine 2011-11-17

This memorandum describes possible emission reduction technologies (ERT) suitable for reducing nitrosamine (NA) emission levels in post combustion capture processes. This memorandum is a continuation of the SINTEF memorandum of 2011-09-20 (Appendix 3).

To control NA emission levels, there are basically five different strategies:

1. Reducing the level of nitrosating agents in the flue gas

2. Reducing the nitrosation reaction rate in the absorption liquid

3. Selective removal/destruction of nitrosamine in the absorption/wash liquid

4. Improving wash efficiencies

5. Selective removal/destruction of nitrosamine in the treated flue gas

In the above mentioned memorandum was concluded that for strategy 1, the reduction of NOx in the flue gas would be a possible option. Technologies for lowering NOx content in flue gas are well known. However, the implications of the kinetic aspects of the equilibrium reaction between NO and NO2 at 100% humidity at temperatures between 40-60°C is less known. If this knowledge would be available, the next step would be the assessment of the feasibility of the available NOx reducing technologies.

Advice: study the kinetic aspects of the reactive absorption of NO2 into an alkaline solution from simulated flue gas and develop a comprehensive model.

Regrading strategy 2, reducing the nitrosation reaction rate, there are several possible options:

a. Removal of nitrite in the absorption liquid

b. Removal of secondary amines

c. Reaction inhibitors

Removal of nitrite in the absorption liquid can be done for example using ion-exchange chromatography. However, this would be very challenging to control the level of nitrite to low contents in a continuous process. Another option can be the destruction of nitrite, e.g. oxidation of nitrite to nitrate. This could be feasible. However, the main challenge would be to prevent the oxidation of the amines during the oxidation step of nitrite to nitrate. Another possible direction is to reduce nitrite by hydrogenation. Hydrogenation of nitrite to nitrogen using hydrogen and palladium type catalyst is well known. One of the main research question would be what is the impact of the hydrogenation of nitrite on the absorption liquid. Regarding the removal of secondary amines, this would strongly depend on the type of absorption liquid if this would be feasible. However, an interesting option is to understand if it is possible to remove volatile secondary amines. A possible option for developing a concept would be based on the stripper condensate.

Regarding reaction inhibitors, there are at this moment several reaction pathways at alkaline conditions for the nitrosation postulated. Based on these pathways, radical scavenger type of inhibitors would not lead to a subsequent lowering of the reaction rate. To develop inhibitors, more insights need to be obtained regarding the reaction pathway. A high throughput screening methodology can lead to a decrease in development time.

Another interesting option would be to examine the possibility to remove reaction promotors (e.g. formaldehyde). This can theoretically be done by removing these components from the stripper condensate and the wash water (adsorption using activated carbon).

Advice:

-study the possibility of polishing the wash water and stripper condensate for volatile secondary amines and lower hydrocarbons.

-study the impact of hydrogenation of nitrite on the degradation of amine

Regarding strategy 3, Selective removal/destruction of nitrosamine in the absorption/wash liquid, in Appendix 3 (the SINTEF memo) several options are already mentioned, ranging from adsorption (e.g. zeolites) to reactive destruction using for example advanced oxidation (wash water), electrochemical reduction (wash water, absorption liquid), hydrogenation and UV. An interesting option would be to conduct the hydrogenation in a contact device whereby the hydrogen is separated from the liquid phase by a very thin layer of catalyst (e.g. Pd) deposited on a micro-porous membrane. This contact method can be easily implemented in a post combustion capture facility. A simple setup for hydrogenation is shown in Figure D-1.


Figure D-1: Test setup at TNO for continuous hydrogenation of nitrosamines

Another possibility would be UV-treatment. UV-treatment on the absorption liquid would, due to the presence of other light absorbing molecules, be less efficient. However, using UV on wash liquid would be straight forward. More details are shown in Figures D2-6. In a next phase proof of concept should be obtained.
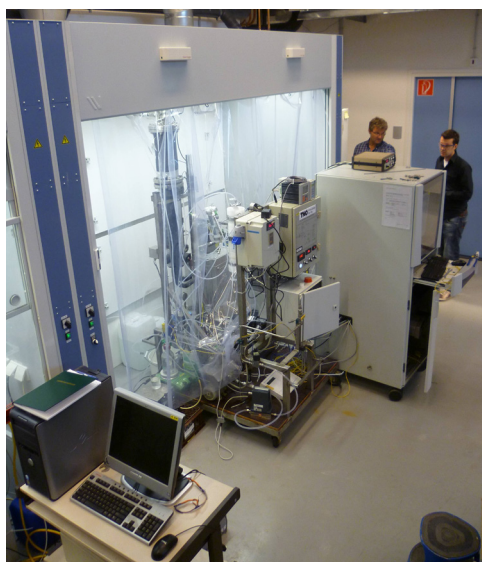
Summary Results TNO UV-Treatment

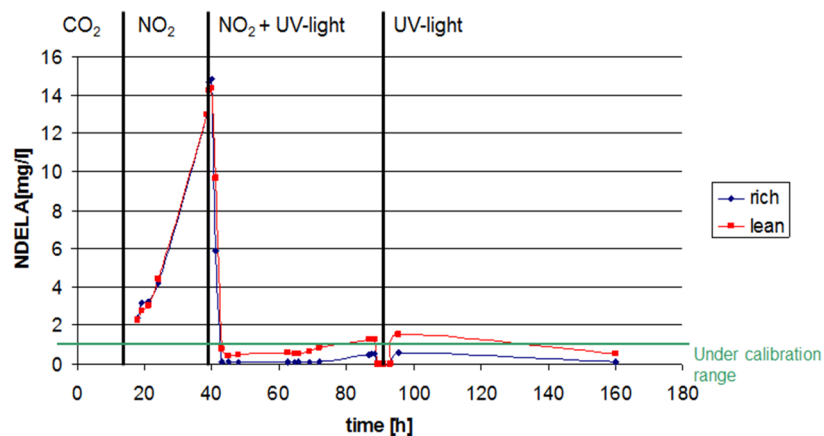**Figure D-2: Laboratorium setup developed to study proof of principle destruction of N-DELA**
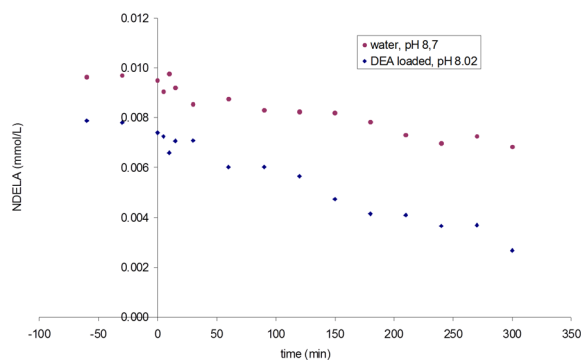
Figure D-3: Relation between UV-treatment and process conditions (temperature, CO2 content, concentration) studied (batchwise)
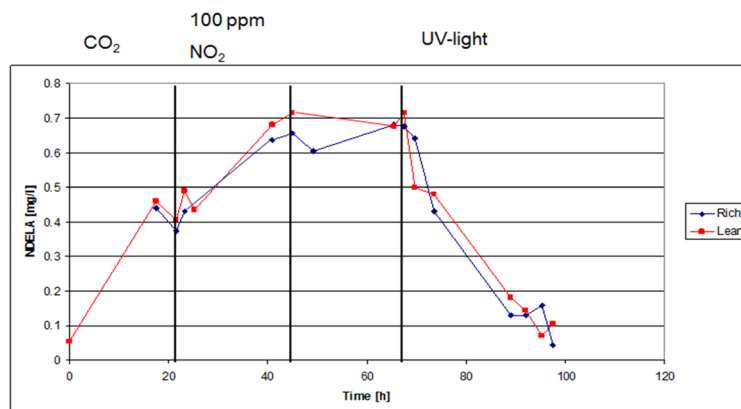

Figure D-4: Continuous setup (absorption-desorption unit) equiped with UV-treatment in the rich liquid

Figure D-5: Experimental results continuous setup (artificial flue gas CO2/air for in total 160 hours), showing proof of principle

Figure D-6: Experimental results continuous setup (artificial flue gas CO2/air for in total 160 hours) using used MEA from Maasvlakte pilot plant, showing proof of principle

PROJECT NO.
801862

REPORT NO.
F21929

VERSION
2

39 of 44

Next to UV-treatment, another interesting possibility is to destroy nitrosamine by UV in the stripper condensate (see text box below).
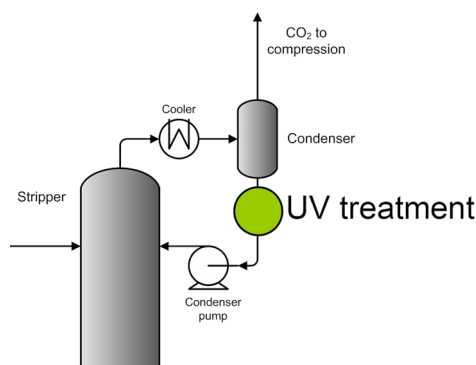

UV-treatment condensate stripper

The amount of emitted NA depends, next to the process conditions, on the volatility of the NA and the interaction with water (wash section). Components, such as NDMA, are for instance very volatile and less polar. Therefore, it is relatively difficult to prevent emissions compared to less volatile and more polar NA (e.g. NDELA).

One way of reducing emissions is UV treatment of the wash liquid or absorption liquid. However, this has the following drawbacks:
- Presence of other components in the absorption liquid can lead to reduced efficiency for UV-treatment
- UV treatment of the washing liquid can be hampered by the relatively higher pH-values due to co-absorption of amines (the kinetics of UV-destruction (photolysis) is dependent on the pH).

Also the lower concentration of NA present in the treated flue gas after the absorber compared to the concentration of NA present in the CO_2 stream at the top of the stripper leads to the thought that it is better address the issue of NA reduction from the stripper side. One interesting concept is to treat the condensate liquid with UV as a mean to destroy nitrosamine (Figure D-7). Due to the high temperature at the top of the stripper relatively significant amounts of NA can be present in the gas phase. In the condenser the temperature is typically lowered from 100 to 30-40°C. As a result water present in the saturated CO_2 stream is condensed. The condensate will contain relatively high amount of NA. The invention is to treat this condensate liquid with UV. It is of importance to note that the condensate has a more favourable pH for UV-destruction (the condensate is saturated with CO_2) than the wash liquid from the absorber.


Figure D-7: UV treatment of the stripper condensate to reduce NA emissions

The UV-treatment can consist of exposing the condensate to UV light in the 200-300 nm range. After UV-treatment, an adsorption stage can be added for further reducing components in the condensate stream. This adsorption stage can make use of for example activated carbon, ion-exchange resins.

Advice:

- Develop proof of principle for selective hydrogenation of nitrosamine using above mentioned contact device.

- Develop proof of concept of UV treatment in a pilot plant operation

Regarding improving wash efficiencies, this can be done using a two stage wash section. The lower wash section is used for the water balance and the removal of amines. The upper wash section is operated iso-kinetically. The wash liquid should consist out of strong oxidizers (destruction of organic components) and a reduced pH (removal of amines and ammonia).
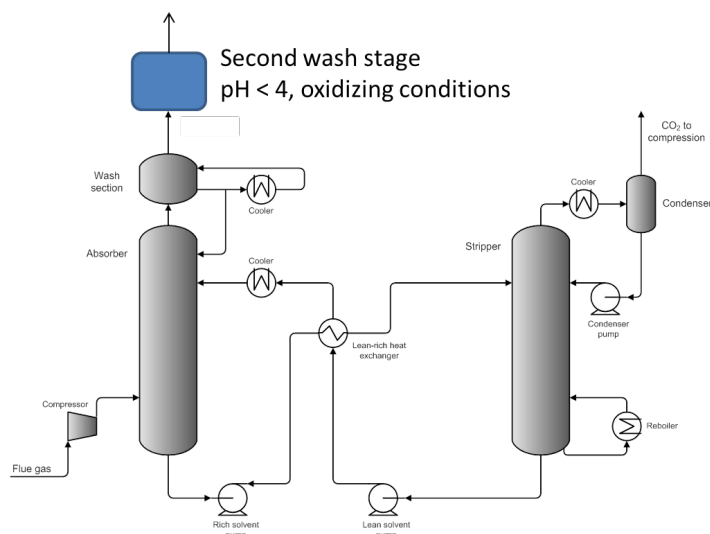
Advice:

- *Develop proof of concept second destructive wash stage*

Regarding the selective removal/destruction of nitrosamine in the treated flue gas, a possibility would be UV-treatment or plasma treatment. For the first option, UV-treatment, this can be considered as theoretically feasible. However, residence times and scale up potential would be the key. This would also be the same for plasma-treatment.

Advice:
Due to foreseen scale up issues, do not start researching this option.

Appendix 5: MEMO TNO Aerosol 2011-11-17

This memorandum describes possible Emission Reduction Technologies (ERT) for the prevention of aerosol formation during post combustion capture. This memorandum refers to the SINTEF memorandum of 2011-9-20.

The issue of aerosol formation in absorption processes for exhaust gas purification is well known. In absorption processes aerosols are formed by spontaneous condensation or desublimation mechanisms in supersaturated gases. Super-saturation of a gas phase is the necessary precondition and the first step of aerosol formation[16][1]. It is of importance to note that super-saturation in absorption processes can be caused by two different mechanisms:

A. Chemical reaction in the gas phase followed by desublimation of the generated component.

B. Crossing the dew point line by simultaneous mass and heat transfer

Here below, the two above mentioned mechanisms are further discussed related to post combustion capture.

Mechanism A:
A classical example for aerosol formation by chemical reaction is the reaction of ammonia (vapour) with HCl acid (vapour), leading to the formation of ammonium chloride (solid). This mechanism can also occur in the post combustion capture processes of CO_2. However, this strongly depends on the gas composition of the, to be treated, flue gas. An example is the presence of SO_2 as a vapour component, reacting with MEA or ammonia present in the gas phase. This example is of relevance for flue gas derived from coal firing. It is of importance to note that for this reaction the presence of water is needed. For coal derived flue gas, typically, the level of SO_2 present as gaseous component would be below 10 ppm. In the very unrealistic case that this SO_2 will react with gaseous MEA or ammonia in the molar ratio of 1 molecule of SO_2 with 2 alkaline molecules substantial amount of aerosols can be formed. However, more realistic is that a large portion of this SO_2 is captured from the flue gas into the absorption liquid. Nevertheless, this mechanism can explain part of the aerosol emission upon treating coal fired derived flue gas. Testing at isothermal conditions in the absorption tower at the Maasvlakte capture plant revealed that this effect is minor.

For flue gas derived from the combustion of natural gas, the amount of acidic molecules such as SO_2 would be very low. Therefore, mechanism A is off les relevance.

Mechanism B:
This mechanism leads to the so-called condensation aerosol. The formation of condensation aerosols is strongly depended on the super-saturation of a gas. It is of importance to note that the saturation ratio must exceed a critical value before molecules can form stable clusters and before nucleation takes place. This critical value depends on the nucleation mechanism. If nuclei are

---

[16][1] K.H. Schaber, Aerosol formation in absorption processes. Chem. Eng. Sci., vol 50, 1995, pp 1347-1360

consisted solely from the condensable components, the mechanism is called homogenous nucleation. If foreign nuclei are present, heterogeneous nucleation can take place.

After nucleation, the aerosols can grow by condensation or coagulation. Basically, the aerosol particles interact by heat and mass transfer.

This mechanism is of relevance for post combustion capture processes. Super-saturation can occur due to the temperature profile over the absorption tower. This temperature profile is created by the reaction heat due the reactive absorption of CO2 and the different inlet temperatures of the, to be treated, flue gas and the lean absorption liquid. In Figure E-1, typical temperature profiles are given which occur on treating flue gas originating from natural gas fired operations.
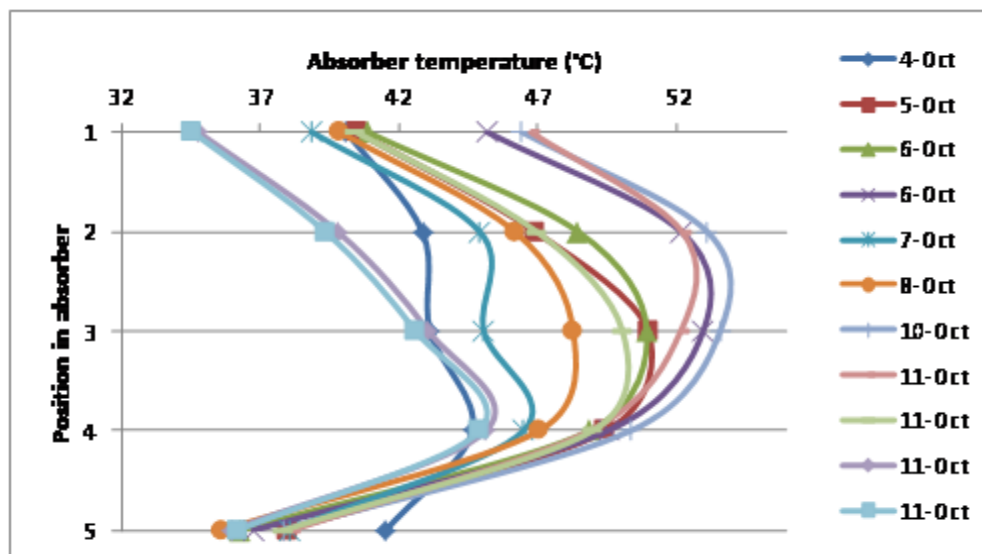

Figure E-1: Examples of a temperature profile in the absorber.

Aerosols would be formed when the flue gas is cooled down in the absorption tower creating the supersaturation. Homogeneous nucleation can occur when there is a high driving force. Factors in favor of creating high driving force are connected with high absorption kinetics and high heat of reaction. Aerosols formed due to heterogeneous nucleation can occur at lower driving forces. To reduce the tendency of the formation of aerosols, the following actions can be taken:

1. reduce the presence of heterogeneous nuclei
2. reduce the temperature bulge [2]

For the first strategy, flue gas clean up is important to reduce particulate matter or in the case of coal fired systems to reduce the presence of SO_3 based aerosols in the to be treated flue gas.

For the second strategy, intermittent cooling or operating at lower gas/liquid ratio or at lower inlet temperatures of flue gas and absorption liquid can be of relevance. It is of importance to study the effect of the super-saturation created by the temperature profile on the aerosol formation.

PROJECT NO.
801862

REPORT NO.
F21929

VERSION
2

43 of 44

Advice:
  Experimental investigation of the influence of the temperature profile on the overall formation of aerosols.

Aerosols can also be formed by mechanical entrainment. However, droplet size is typically larger than aerosols formed due to the above mentioned reasons. Droplet created by mechanical entrainment can be readily by conventional demisters. Design of the absorption tower and the surface tension of the absorption liquid are important influences for mechanical entrainment. To study mechanical entrainment, pilot plant operation at condition of no CO_2 capture (ie isokinetic operation of the absorption tower) would be an interesting option.

Advice:
  Experimental investigation of mechanical entrainment at isokinetic operation of the absorption tower.

The sections below describe the technical options for the removal of aerosols from the treated flue gas. After formation, aerosols are difficult to remove from the treated flue gas. Typical options are:

  - filtration
  - electrostatic scrubber

Filtration has been studied in this project by the Brownian Diffusion Unit (BDU). The main conclusion from the work is that this is feasible. However, scaling up can be an issue. Typically, a pressure increase of the treated flue gas of 50 mbar is needed to overcome the pressure drop over the BDU. For a 430 MW NGCC plant, this would lead to an additional energy consumption of the blower of 4,3 MWe to in total 11,7 MWe. Next to this energy consumption, integration of the BDU and capital expenditure can be an issue.

Electrostatic scrubber (eg wet electrostatic precipitator (WESP)) is an interesting alternative. Although scaling up issues can be an issue. Electrostatic scrubber systems can be considered as mature technologies.

Advice:
  - *Economic evaluation for large scale application of BDU*
  - *Technical evaluation of electrostatic scrubber*

An interesting concept for the reduction of MEA emission by aerosol could be the use of an acid wash scrubber. It is of importance to note that this only will work, if the MEA is present as MEA and not as a salt. This is the case for post combustion for NGCC plants and predominantly the case for pulverized coal based power plants. Normally, wash systems would not be useful for the removal of aerosols. This is still the case for an acid wash system. However, what will happen is that the MEA is removed by the acid wash from the vapour phase. Due to the fact that MEA is removed from the vapour phase, the free MEA present in the aerosols (typically in the concentration of 1 mol/L) will be absorbed in the acid wash via the vapour phase. Due to the fact that by using an acid was there is an infinitive enhancement factor. This implies that the removal of MEA from the vapour phase is gas

PROJECT NO.
801862

REPORT NO.
F21929

VERSION
2

44 of 44

phase controlled. Aerosols will have a high surface are per volume, meaning that the mass transfer from the aerosol phase to the vapour phase would be rather high. A caveat is that the aerosols it self will not be removed by an acid wash, only the content of MEA will be strongly reduced. An acid wash is also recommended for the removal of ammonia.

Advise:
- Experimental verification of the use of an acid wash, not only for the reduction of ammonia emission but also for the reduction of MEA emission via aerosols.