SINTEF REPORT

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TITLE

Emission Reducing Technologies
H&ETQP Amine6

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Contract No: 257430119

REPORT NO. SINTEF A18095	CLASSIFICATION Unrestricted	CLIENTS REF. David Grainger	
CLASS. THIS PAGE Unrestricted	ISBN 9788214050240	PROJECT NO. 801573	NO. OF PAGES/APPENDICES 97/5
ELECTRONIC FILE CODE I:\prosjekt\8040Prosessteknologi\MK801573_AMINE6_HKO\Adm\Notater_Rapporter\Rapporter HETQP Amine 6 Final unrestricted report.docx		PROJECT MANAGER (NAME, SIGN.) Herman Kolderup Herman Kolderup	CHECKED BY (NAME, SIGN.) Paal Skjetne
FILE CODE	DATE 2011-02-14	APPROVED BY (NAME, POSITION, SIGN.) Ole Wærnes, Research Director Ole Wærnes	

ABSTRACT

The present work has assessed technologies to reduce toxic emission from CO_2 capture plants. This emission includes the amines and its degradation products except ammonia. We believe the water wash will be a central part of the emission control process. For solvents such as MEA an appropriate water wash system will most probably bring emission concentration level of MEA below 1 ppmv. We believe acid wash technology is the first option that should be considered if there is a need to obtain lower gaseous emission levels. Acid washes are apparently efficient for ammonia scrubbing, and we expect comparable efficiency for most amine components.

Only pertinent and thoroughly performed laboratory and pilot experiments will demonstrate reliable emission levels of nitrosamines and nitramines. If it is found that these emission levels are too high, we would recommend the use of UV-light in combination with water-wash and acid-wash. The simplest use of UV-light would be treating the liquid phases in the water-wash and/or acid-wash and thereby reverse the formation of nitrosamines and/or nitramines. If the acid wash and UV-treatment is integrated properly, almost all potential nitrosamines, nitramines and nitrosamine/nitramine precursors could be captured in the acid-wash. The more demanding option would be to use UV light to treat the flue gas coming through the water wash. The main issue may be the residence time needed for a UV process.

Total emission concentration level of a pollutant in both gas phase and dispersed liquid phase can be expressed in terms of mol fraction in ppm unit. We believe a combination of water-wash, acid-wash and demisters could be utilized to achieve a total emission concentration level of 0.2 ppm of solvents such as MEA. Efficient demisters are needed to achieve appropriate control of droplet emissions. If sub-micron mist and aerosols are found to contribute significantly to total emissions, more advanced demisters/filters should be considered.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Chemical engineering	Kjemiteknikk
GROUP 2	Gas cleaning	Gassrensing
SELECTED BY AUTHOR	Carbon capture	Karbonfangst
	Amine solvents	Aminoppløsninger
	Emission reduction	Utslippsbegrensning

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Summary

The present work has assessed several emission reducing technologies (ERT) that can be applied in amine based CO_2 capture plants. The emissions include the amines and its degradation products except ammonia. We believe the water-wash will be a central part of the emission control process. For solvents such as MEA an appropriate water wash system will most probably bring emission concentration level of MEA below 1 ppmv. We believe acid wash technology is the first option that should be considered if there is a need to obtain lower gaseous emissions. Acid washes are apparently efficient for ammonia scrubbing, and we expect comparable efficiency for most amine components.

Only pertinent and thoroughly performed laboratory and pilot experiments might demonstrate reliable emission levels of nitrosamines and nitramines. If it is found that these emission levels are too high, we would recommend the use of UV-light in combination with water-wash and acid-wash. The simplest use of UV-light would be treating the liquid phases in the water-wash and/or acid-wash and thereby reverse the formation of nitrosamines and/or nitramines. If the acid wash and UV-treatment is integrated properly, almost all potential nitrosamines, nitramines and nitrosamine/nitramine precursors could be captured in the acid-wash (the UV reversing the nitrosamines and nitramines to amines that will bind in an acid wash). The more demanding option would be to use UV light to treat the flue gas coming through the water wash. The main issue may be the residence time needed for a UV process.

Simulation results show that for MEA it is possible to go very low in terms of gaseous emission concentration level, even to the low level of 0.01- 0.2 ppmv. These results also show that the number of stages is most important then the gas temperature and finally the amount of water (β).

For AMP low temperatures combined with two washing stages and high amount of water is needed to achieve an emission level below 1 ppmv. The effect of using one more stage is substantial and should be recommended for this amine. AMP is much more difficult to capture in a water wash compared to Piperazine even if the vapour pressure for the pure components is lower. The reasons are large difference in activity coefficient and loading. The same is even more the case when comparing AMP to MEA.

Total emission level of a pollutant in both gas phase and dispersed liquid phase can be expressed in ppm, when ppm means number of moles of a pollutant in both gas phase and dispersed liquid phase relative to the total number of moles of all substances in the gas phase.

The simulations do not include any liquid entrainment. Amount of aerosol formation in the absorber and its penetration through water wash sections including the demisters can not be calculated. It is not unreasonable conservative to assume that MEA in the aerosol emission from a new plant can contribute in the order of 0.1 – 0.2 ppm MEA to the total emission of MEA even after two stages of water wash including demisters. However, in the absence of experimental data or a model it is difficult to come up with a scientific justification of this assumption.

Properly dimensioned standard demister units are needed to achieve appropriate control of droplet emissions.

We believe a combination of water-wash, acid-wash and demisters could be utilized to achieve a total emission concentration level of 0.2 ppm of solvents such as MEA. If sub-micron mist and aerosols are found to contribute significantly to emissions, more advanced demisters/filters should be considered.

There are a number of other ERT options based on ionization of the gas phase, introduction of ozone and UV treatment. Such technologies do in principle seem promising, but further studies would be required to determine if they can give significant emission reductions at a reasonable cost.

Other technologies based for example on combustion of degradation products appear to be less suitable for the gas streams encountered in a CO_2 capture plant.

A maturity assessment and benchmarking of water wash, chemical wash and demister systems applied in amine based CO_2 capture plants have been performed using systematic DNV methodology. Available information on lesser known ERT for application in such CO_2 capture plants has been insufficient for performance and maturity evaluations based on DNV methodology.

Even for two washing sections it is still uncertain to what extent the targeted concentration emission levels can be reached. Consequently further research and investigations are needed in order to improve the reliability of the conclusions in this report. We recommend main efforts to be put on the following subjects in the extended work:

1. Evaluation and selection of test facilities
2. Evaluation and selection of emission measurements methods
3. Emission measurements from absorber demister units and water wash sections in test facilities including pilot plants. Measurements includes sampling and analysis of total amine content in gas flow including degradation products
4. Verification and measurement of fog formation including qualitative continuous registration of mist and fog
5. Validation of simulation results from CO2SIM
6. Validation of gas liquid equilibrium data on very low partial pressure
7. Sampling and analysis of non-volatile tracers added to the absorbent solution in order to validate droplet entrainment from absorber solution
8. Sampling and analysis of non-volatile tracers added to the first water wash stage in order to validate droplet entrainment from water wash solution
9. Gathering of data from industrial plants

1. INTRODUCTION

1.1 The CO_2 capture plant at Mongstad

The "Energiverk Mongstad" (EVM) project consists of a gas pipeline from Kollsnes to Mongstad, a Combined Heat and Power (CHP) plant and refinery modifications (primarily crude unit). The CHP plant will be located at the Mongstad Refinery site, north of Bergen in Norway.

In connection with the concession and emission permit for the EVM project, an agreement (“the Implementation Agreement") on CO_2-handling at Mongstad was signed between Statoil and the Norwegian State. The agreement states that CO_2 shall be captured from CHP flue gas in a large-scale capture plant, with a planned investment decision in 2012. The approximately 1.3 million tonnes per year of CO_2 in the CHP flue gas is the basis and the captured CO_2 will be sent to geological storage under the Norwegian Continental Shelf.

The CO_2 Capture Mongstad project has now been started and is in an early development phase. The project is at the moment organized as a joint project between Gassnova SF and Statoil ASA. The purpose of the project is to plan and build a large-scale CO_2 capture plant based on amine capture technology.

An amine based CO_2 capture plant may have potentially harmful emissions to the atmosphere. Particularly amines and degradation products from reactions in the process and in the atmosphere are of concern. There is limited knowledge about the behaviour of these chemical compounds. Thus several studies have been initiated by the project to increase this knowledge.

This particular study (Amine 6) concerns the emission reducing technologies that can be implemented in the capture plant. Amine 6 includes concentration estimates of chemical compounds that might harm health and environment. The concentration estimates is made down stream the packing elements of a typical amine based CO_2-absorber. Technologies which can reduce the emission of such compounds from the CO_2-absorber are identified and assessed.

1.2 Objectives

This study shall identify and document the technology status for emission reducing technologies related to emissions of amines and other undesirable components in the exhaust gas leaving the capture plant absorber.

There are three main objectives in this study:

1. Estimate vapour and entrained liquid loads in a typical amine-based absorber
2. Identify emission-reducing technologies that can reduce the emission concentration level* of amines from the absorber down to:
    i. 0.2 - 1 ppmv
    ii. 0.01-0.2 ppmv
3. Document and assess the technology maturity of the Emission Reducing Technologies (ERT) that are likely to meet the emission targets and assess the implications of these ERTs on process performance for the capture facility

   Document technology status for all identified technologies, industrial references, test facilities, potential technology improvements, scale-up issues, mechanical limitations and process implications

The three objectives are referred to as work packages WP1, WP2 and WP3 in this report.

* These are normally vapour concentrations expressed as volume fractions multiplied by one million, which are identical to molecular fractions multiplied by one million and can be converted to partial pressures by multiplying with total pressure and dividing by one million. Unlike concentrations in liquid, the unit ppmv is normally identical to the unit ppm for gas concentrations. Exception is when ppm means number of moles of a pollutant in both gas phase and dispersed liquid phase relative to the total number of moles of all substances in the gas phase.

Concentrations of liquid and solid particles dispersed in a gas phase are normally calculated in terms of mass per volume gases expressed in mg/Nm^3 or $mg/Nm^3(dry)$. The letter N refers to gas conditions at standard conditions: Temperature 273 °K and pressure 101.3 kPa. Dry means volume gases calculated deducting the water vapour volume. Such mass concentrations can be converted to ppm as follows:

$ppm = (mg/Nm^3) \cdot V_{NM}/M = (mg/Nm^3(dry)) \cdot X(dry) \cdot V_{NM}/M$ X(dry) = Dry gas volum fraction

V_{NM} = Mol. volume at standard conditions = 22.414 $Nm^3/kmol$. M = Mol. weight of pollutant kg/kmol

According to DIRECTIVE 2001/80/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2001 on the limitation of emissions of certain pollutants into the air from large combustion plants, emission limit values (ELV) should be calculated in $mg/Nm^3(dry)$ assuming an oxygen content by volume in the waste gas of 3 % in the case of liquid and gaseous fuels, 6 % in the case of solid fuels and 15 % in the case of gas turbines.

1.3 Rationale for joint SINTEF and DNV work

The rationale for the joint effort by SINTEF and DNV relates to the totality of the above mentioned objective. It is foreseen that combining the methodology and experience of technical risk management, provided by DNV, with the scientific expertise provided by SINTEF, will utilize the complementary skills of each of the companies, and enhance the quality of the project. In particular, the complementary skills apply for the following aspects:

- In order to define and select relevant activities, the systematic DNV methodology in chapter 4 in this report and the expertise provided by SINTEF will enable a cost-efficient selection of qualification methods, attacking the relevant failure modes of concern

- New research activities should be selected and optimized to fit in with the totality of qualification efforts that will be needed to provide the necessary evidence that the ERT will function according to defined functional expectations. This means that experimental efforts by SINTEF can be optimized in accordance with the technology qualification provided by DNV.

After completing this report there is an option for extending the scope of work to include potentially more accurate analysis and experimental testing or other qualification activities in order to increase the accuracy and confidence in the technology assessment.

2. VAPOUR AND ENTRAINED LIQUID FROM ABSORBER

2.1 Absorber modelling (WP 1a)

2.1.1 Summary scope of service and objectives

The following specifications are taken from GASSNOVA's call for tender document H&ETQPAmine6. The flue gas data in table 2.1 and the solvent conditions in table 2.2 are used as basis for this work.

The flue gas is cooled in a direct contact cooler (DCC), which is located upstream the absorber. The flue gas exiting the direct contact cooler will be saturated with water.

Table 2.1 Flue gas conditions

Property	Place of measurement	Value
Temperature (°C)	Inlet DCC	120
	Inlet absorber	25-45
Pressure (bara)	Inlet DCC	1.01
Gas flow (t/h)		1550
Gas composition	Component	
(mol %)	CO_2	3.4
	N_2	76
	O_2	13.8
	H_2O	6.8
(ppmv)	NO_x	3
	NH_3	2

Table 2.2 Solvent conditions

Property		**Solvent A (MEA)**[1]	**Solvent B (AMP)**[2]
Composition excluding CO_2 (wt %)	Amine	30	25
	Piperazine PZ	0	15
	Water	69	60
	Heat stable salts	1 %	
CO_2 content (mol CO_2/mol amine)	Lean loading	0.22	0.15
	Rich loading	0.46	0.64
Temperature °C		25 - 40	25 - 40

1 Monoethanolamine, 2 Methylaminopropanol

SINTEF simulated the cooling of the flue gas in a direct contact cooler to provide the temperature presented in table 2.1, and used the resulting saturated gas composition for modelling the absorber operation. The implications of variations in solvent loading and composition is described and discussed, see the sections below.

The amine vapour concentration and liquid carryover is estimated for a typical absorber configuration with gravity fed distributors and structured packing. *SINTEF has based the simulations on a suggested typical absorber design for these gas flow rates.* These estimates shall thus be used as basis for evaluating emission reduction technologies and proposing optimal operating and column internal configurations.

2.1.2 Determining the size of the absorber

The packing height was set to 15 meter which will for MEA give a reasonable capture rate and loading of the solvent. A higher packing height would increase net absorption rate but capital cost will also increase rapid. Total absorber column height is roughly a factor of two of the packing height due the size of liquid distributors, sump, gas/liquid pipes and water wash sections. Hence a packing height of 15 meter is a good balance between capture rate and capital cost, but may not be the optimal height.

Absorber diameter was calculated based on two inlet superficial gas velocities 2 and 3 m/s which correspond to 16.2 and 13.2 meter. These two velocities were selected to investigate the effect of vapour load and amine loss.

2.1.3 Description of simulation method absorber modelling

The simulation work in WP 1A was simulated with CO2SIM v4.1.04. This is SINTEF's own software for post combustion CO_2 capture. It is an established commercial quality simulator and includes rigorous thermodynamic and rate models.

The thermodynamics chosen for solvent A was the "ordinary" - Electrolyte Non-Random Theory (o-eNRTL) model. This is a rigorous full speciation activity model that gives activity coefficients for all main components in the solution, more information regarding this model as well as CO2SIM implementation can be found in ref.[1]

A "soft" modelling approach was used for solvent B due the complex nature of this system and the lack of available laboratory data. This soft model was also extrapolated for solvent B at temperature below 40 °C The vapour pressures resulting at the top of the absorber for solvent B is thus uncertain at these conditions. A screen shot of the software used is shown in figure 2.1

The "soft" modelling approach refers to a method for describing the CO_2 equilibrium partial pressure (fugacity) by using a simplified model to fit the VLE data for new solvents, in particular, Solvent B, as well as some simplified physical property models. It has shown to give reliable results when investigating energy requirements for CO_2 capture processes. However, when investigating amine losses, it is not known what the deviations in estimating the fugacity are for low concentration amine solvents, i.e in the water wash sections. In any case, the most important models for evaluation amine vapour losses are the partial pressure correlations of the solvent itself and the gas film resistance model, not only the CO2 VLE model. It is therefore concluded that the soft modelling approach is applicable for this purpose.

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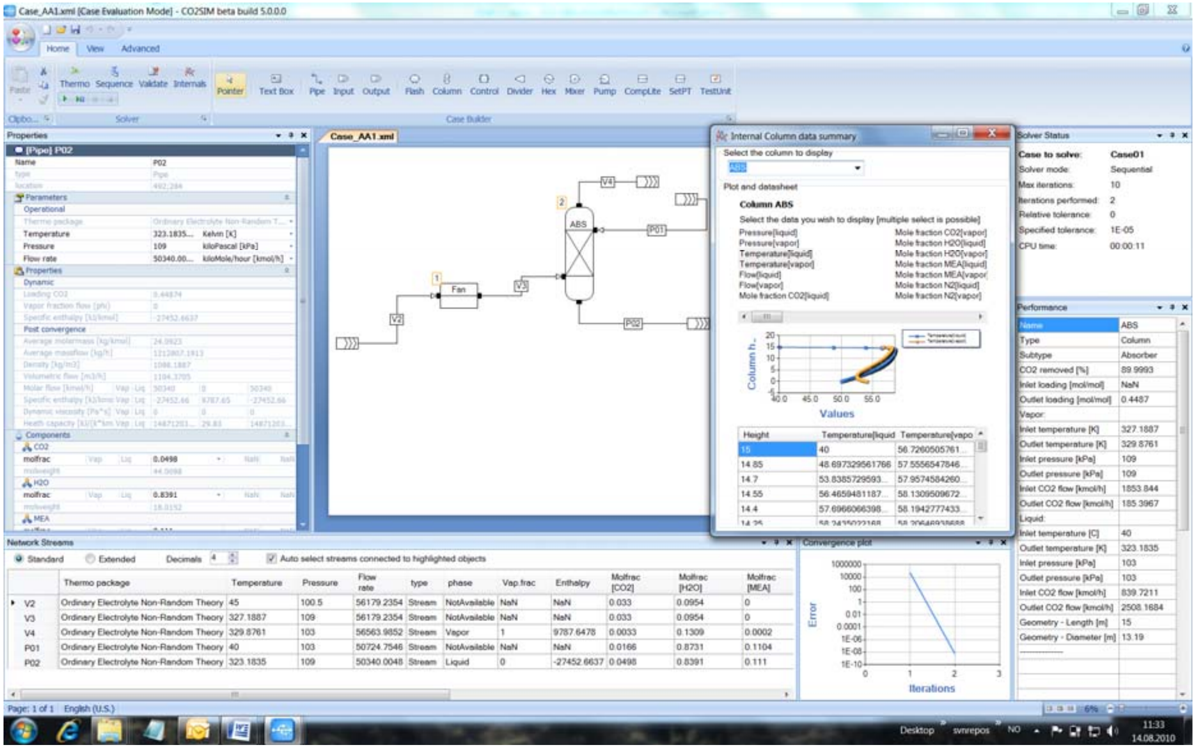
[1] Hessen, E. T. et al.:"Thermodynamic models for CO2 absorption", Doctoral Thesis, Norwegian University of Science and Technology (NTNU), Department of Chemical Engineering, June 21. 2010

The simulations were performed in a way such that 90 % CO_2 was removed from the flue gas for all cases by using an outer adjust algorithm from the optimization package in CO2SIM. This ensured a good basis for comparison for the different operation conditions.

A flow sheet of the capture process from CO2SIM is given in figure 2.2. Simplification was done by simulation the DCC as a simple flash to specified temperature.

- Fan: Outlet pressure of 1.09 bara
- DCC: Two cooling temperatures 25 °C and 45 °C
- Absorber diameter: Gas velocity set to 2 and 3 m/s which correspond to 16.2 m and 13.2 m in diameter
- Loading: three different loadings for each solvent(see result tables)
- Outlet absorber: 1.03 bara
- Packing: Mellapak 250.Y structured packing from Sulzer Chemtech
- Absorber Packing height set at 15 meter



Properties

[Pipe] P02

Name	P02	
Temperature	323.1835...	Kelvin [K]
Pressure	109	kiloPascal [kPa]
Flow rate	50340.00...	kiloMole/hour [kmol/h]

Components

CO2 molfrac 0.0498

H2O molfrac 0.8391

MEA

Internal Column data summary

Select the column to display: ABS

Plot and datasheet

Column ABS

Select the data you wish to display [multiple select is possible]

Pressure[liquid]
Pressure[vapor]
Temperature[liquid]
Temperature[vapor]
Flow[liquid]
Flow[vapor]
Mole fraction CO2[liquid]
Mole fraction CO2[vapor]
Mole fraction H2O[liquid]
Mole fraction H2O[vapor]
Mole fraction MEA[liquid]
Mole fraction MEA[vapor]
Mole fraction N2[liquid]
Mole fraction N2[vapor]

Height	Temperature[liquid	Temperature[vapo
15	40	56.7260505761...
14.85	48.697329561766	57.5556547846...
14.7	53.8385729593...	57.9574584260...
14.55	56.4659481187...	58.1309509672...
14.4	57.6966066398...	58.1942777433...

Solver Status

Case to solve:	**Case01**
Solver mode:	Sequential
Max iterations:	10
Iterations performed:	2
Relative tolerance:	0
Specified tolerance:	1E-05
CPU time:	00:00:11

Performance

Name	ABS
Type	Column
Subtype	Absorber
CO2 removed [%]	89.9993
Inlet loading [mol/mol]	NaN
Outlet loading [mol/mol]	0.4487
Vapor:	
Inlet temperature [K]	327.1887
Outlet temperature [K]	329.8761
Inlet pressure [kPa]	109
Outlet pressure [kPa]	109
Inlet CO2 flow [kmol/h]	1853.844
Outlet CO2 flow [kmol/h]	185.3967
Liquid:	
Inlet temperature [C]	40
Outlet temperature [K]	323.1835
Inlet pressure [kPa]	103
Outlet pressure [kPa]	103
Inlet CO2 flow [kmol/h]	839.7211
Outlet CO2 flow [kmol/h]	2508.1684
Geometry - Length [m]	15
Geometry - Diameter [m]	13.19

Network Streams

● Standard ○ Extended Decimals 4 ☑ Auto select streams connected to highlighted objects

	Thermo package	Temperature	Pressure	Flow rate	type	phase	Vap.frac	Enthalpy	Molfrac [CO2]	Molfrac [H2O]	Molfrac [MEA]
V2	Ordinary Electrolyte Non-Random Theory	45	100.5	56179.2354	Stream	NotAvailable	NaN	NaN	0.033	0.0954	0
V3	Ordinary Electrolyte Non-Random Theory	327.1887	109	56179.2354	Stream	NotAvailable	NaN	NaN	0.033	0.0954	0
V4	Ordinary Electrolyte Non-Random Theory	329.8761	103	56563.9852	Stream	Vapor	1	9787.6478	0.0033	0.1309	0.0002
P01	Ordinary Electrolyte Non-Random Theory	40	103	50724.7546	Stream	NotAvailable	NaN	NaN	0.0166	0.8731	0.1104
P02	Ordinary Electrolyte Non-Random Theory	323.1835	109	50340.0048	Stream	Liquid	0	-27452.6637	0.0498	0.8391	0.111

Figure 2.1 Screenshot of the CO2SIM simulator

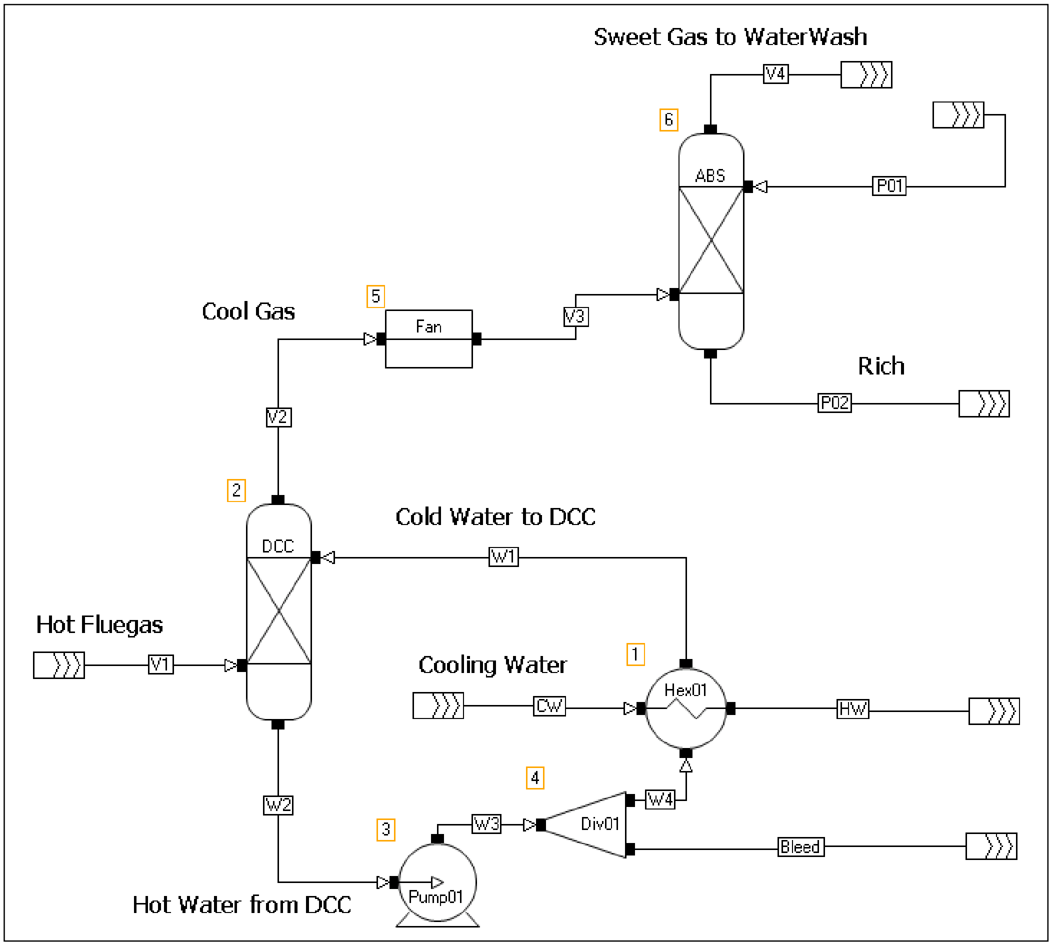


Figure 2.2 Flow-sheet of DCC and absorber

2.1.4 Results and discussion of absorber modelling

Solvent A (MEA)
In table 2.3 and 2.4 the results are shown for the different loadings and temperatures. Elucidations of variations in solvent loading and solvent compositions is described and discussed below.

From the two tables it is shown that, in general, the MEA loss to vent is reduced with higher CO_2 loading of liquid in to the absorber and at lower solvent inlet temperature to the absorber. This is as expected. The higher the loading the less free MEA is available in the liquid solution to exercise its vapour pressure. At lower temperature the vapour pressure is reduced.

It can also be seen that comparing cases AA and AB, there is hardly any differences in the outlet vapour losses as the vapour superficial velocity changes. This is due since the simulator does not predict entrainment in the vapour phase.

The gaseous concentration of MEA from solvent A in gas leaving the absorber is between 43- and 155 ppm respectively at an inlet lean loading of 0.25 and temperature of 25 °C and inlet lean loading of 0.15 and temperature of 40 °C. To maintain proper water balance the inlet absorber pre-cooling duty was adjusted accordingly. It varied from 45 °C to 25 °C.

By further looking at the data it is shown that the gas outlet temperature from the absorber was for the best case BA3, 45.6 °C. Since the inlet temperature was 25 °C, a difference of almost 20 °C, the vapour is not at phase equilibrium with the inlet solvent. This is due to the rate determining heat transfer coefficient between the liquid and vapour phases is low. There is quite some uncertainty as to the value of this coefficient at the given operation conditions. At higher absorber heights the vapour outlet will be closer to equilibrium. It has been shown in different pilot plants that the temperature difference can be large.

In figure 2.3 the absorber internal temperature profiles are shown. Some important points can be pointed out; the low lean solvent loading causes a very large and fast temperature rise at the absorber top. It is so fast that as the vapour is flowing upwards towards the top, it cannot follow the temperature as it rapidly *decreases* towards the solvent inlet. The result is the large temperature difference. This also means that the amine slippage is not at phase equilibrium at the absorber top. This is clearly shown in figure 2.4, showing internal equilibrium vapour pressure and actual vapour pressures in the column. An additional washing unit at the absorber top will thus be able to remove much more of the amine.

The water wash works to a large extent as a cooler and to facilitate mass transfer by providing further contact time to reach equilibrium. In this example, of one assumed that the phases reached equilibrium (a commonly used assumption or, the heat transfer coefficient being infinite, the partial pressure of MEA out would have been 46 kPa as opposed to 160 kPa).

It can also be seen that for Case AA the pre-cooling of the vapour flue causes a temperature crossover at about 2 meters from the bottom of the column causing vaporization and cooling of the liquid phase.

Table 2.3 Absorber performance using solvent A (MEA)

CASE	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
Lean solvent temperature [°C]	**40**	**40**	**40**	**40**	**40**	**40**	**25**	**25**	**25**	**25**	**25**	**25**
DCC outlet gas temperature [°C] [a]	**45**	**45**	**45**	**45**	**45**	**45**	**25**	**25**	**25**	**25**	**25**	**25**
Column diameter [m]	**13.2**	**13.2**	**13.2**	**16.2**	**16.2**	**16.2**	**13.2**	**13.2**	**13.2**	**16.2**	**16.2**	**16.2**
Lean solvent loading [mol CO_2/mol amine]	**0.150**	**0.200**	**0.250**	**0.150**	**0.200**	**0.250**	**0.150**	**0.200**	**0.250**	**0.150**	**0.200**	**0.250**
Lean solvent flow rate [tonne/h]	1176	1457	1981	1074	1297	1667	1157	1384	1743	985	1166	1436
Lean solvent density [tonne/m^3]	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05
Lean solvent flow rate [m^3/hr]	1120	1388	1886	1023	1235	1587	1102	1318	1660	938	1110	1367
Packing height [m]	15	15	15	15	15	15	15	15	15	15	15	15
Rich solvent temperature [°C]	50.03	50.11	50.38	49.67	49.74	49.96	31.99	32.49	33.48	30.94	31.32	32.07
Rich solvent loading [mol CO_2/mol amine]	0.449	0.445	0.432	0.477	0.474	0.467	0.455	0.457	0.456	0.507	0.505	0.500
Flue gas flow [1000 Nm^3/h]	1 222	1 222	1 222	1 222	1 222	1 222	1 222	1 222	1 222	1 222	1 222	1 222
Flue gas temperature DCC inlet [°C]	120	120	120	120	120	120	120	120	120	120	120	120
Flue gas pressure DCC inlet [kPa]	101	101	101	101	101	101	101	101	101	101	101	101
Abs. inlet CO_2 content [mol % wet]	3.30	3.30	3.30	3.30	3.30	3.30	3.53	3.53	3.53	3.53	3.53	3.53
Abs. inlet H_2O content [mol % wet]	9.54	9.54	9.54	9.54	9.54	9.54	3.14	3.14	3.14	3.14	3.14	3.14
CO_2 recovery [%]	90	90	90	90	90	90	90	90	90	90	90	90
CO_2 captured [tonne/h]	73.4	73.3	73.4	73.4	73.3	73.2	73.3	73.3	73.4	73.3	73.3	73.4

a. High pressure fans upstream absorber increase gas temperature by 8 °C

Table 2.4 Gas concentration of MEA between the absorber section and the water wash using solvent A

CASE[a]	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
Outlet gas pressure [kPa]	103	103	103	103	103	103	103	103	103	103	103	103
Outlet gas flow [kmol/h]	56 565	56 339	55 880	56 692	56 517	56 215	52 619	52 441	52 107	52 810	52 687	52 472
Outlet gas temperature [°C]	56.7	56.7	56.6	56.6	56.7	56.7	45.8	45.9	45.6	45.7	45.9	46.0
Outlet gas temperature [K]	329.9	329.9	329.8	329.8	329.8	329.8	319.0	319.0	318.7	318.9	319.0	319.1
Gas concentration of MEA [ppmv]	**155**	**134**	**110**	**155**	**134**	**113**	**63**	**54**	**43**	**64**	**55**	**46**
CO$_2$ content [mol fraction]	0.003	0.003	0.003	0.003	0.003	0.003	0.004	0.004	0.004	0.004	0.004	0.004
Water content [mol fraction]	0.13	0.13	0.12	0.13	0.13	0.13	0.07	0.06	0.06	0.07	0.07	0.06
Inert gas content [mol fraction]	0.87	0.87	0.88	0.86	0.87	0.87	0.93	0.93	0.94	0.93	0.93	0.93
Water saturation pressure [kPa]	17.1	17.1	17.0	17.0	17.0	17.1	10.0	10.0	9.9	9.9	10.0	10.1
Molar gas density [kmol/m^3]	0.038	0.038	0.038	0.038	0.038	0.038	0.039	0.039	0.039	0.039	0.039	0.039
Outlet gas volume flow [1000 m^3/h]	1 506	1 500	1 487.5	1 509	1 505	1 497	1 355	1 351	1 341	1 359	1 357	1 352
Outlet gas velocity [m/s]	3.06	3.05	3.02	2.04	2.04	2.03	2.75	2.75	2.73	1.84	1.84	1.83

a. See table 2.3 for the different process conditions used in simulations

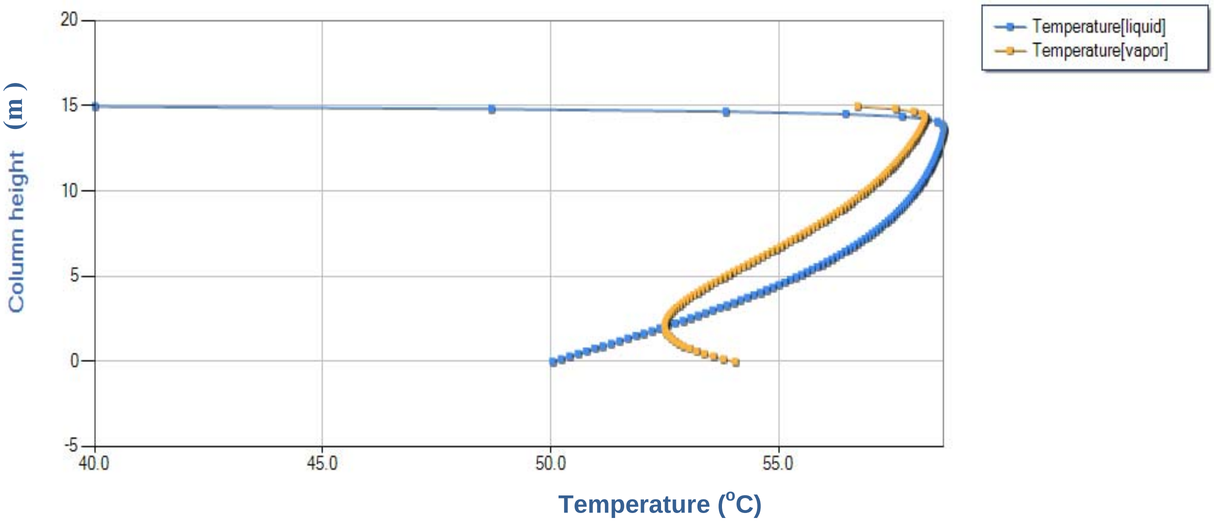


Figure 2.3 Internal temperature profiles for liquid and vapour phases for solvent A case AA1

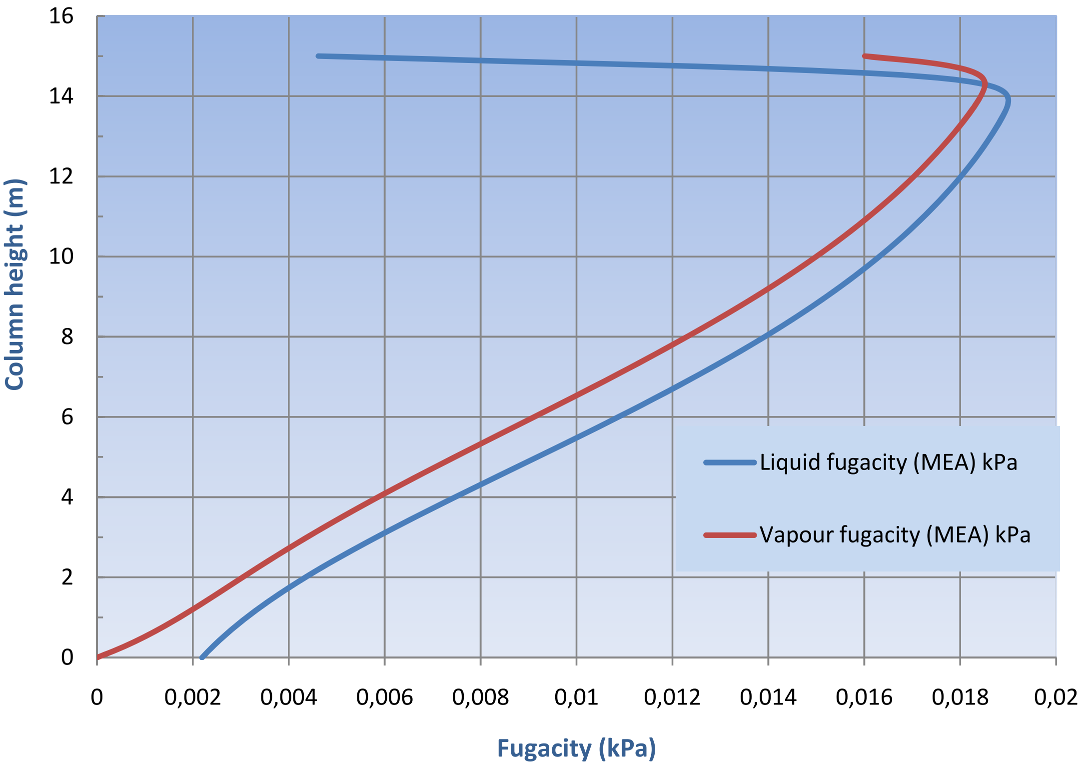


Figure 2.4 Internal vapour pressure profiles for solvent A for case AA1 equilibrium and actual column height (m) vs vapour pressure (kPa)

Solvent B

Results are shown for the different loadings and temperatures of solvent B in the next tables followed by an elucidative description and discussion of variations in solvent loading and solvent compositions.

By comparing the tables for both solvents, it is shown that the trends are similar. However, the amount of solvent slippage out of the absorber is higher for solvent B.

Simulation BA3 shows a value of 217 ppm out of the absorber top before any washing occurs. This is about 4 times more than for MEA. It should be noted that the vapour pressure correlations in the simulator for the solvent is based on pure AMP. In our modelling approach, the activity coefficient is therefore set to unity; however, the free AMP in solution is based on how much it is CO_2 loaded. The higher the loading, the less free AMP is available for contributing to the vapour pressure. AMP has a higher vapour pressure compared to piperazine. In the blend it is thus expected that the amount is somewhat lower.

Table 2.5 Absorber performance using solvent B (AMP + PZ)

CASE	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
Lean solvent temperature [°C]	**40**	**40**	**40**	**40**	**40**	**40**	**25**	**25**	**25**	**25**	**25**	**25**
DCC outlet gas temperature [°C] [a]	**45**	**45**	**45**	**45**	**45**	**45**	**25**	**25**	**25**	**25**	**25**	**25**
Column diameter [m]	**13.2**	**13.2**	**13.2**	**16.2**	**16.2**	**16.2**	**13.2**	**13.2**	**13.2**	**16.2**	**16.2**	**16.2**
Lean solvent loading [mol CO_2/mol amine]	**0.10**	**0.15**	**0.20**	**0.10**	**0.15**	**0.20**	**0.10**	**0.15**	**0.20**	**0.10**	**0.15**	**0.20**
Lean solvent flow rate [tonne/h]	818	924	1059	818	924	1059	598	655	725	597	655	725
Lean solvent flow rate [m^3/hr]	779	880	1009	779	880	1009	569	624	691	569	624	690
Packing height [m]	15	15	15	15	15	15	15	15	15	15	15	15
Rich solvent temperature [°C]	49.94	49.91	49.88	49.94	49.91	49.88	29.91	29.92	29.96	29.91	29.93	29.98
Rich solvent loading [mol CO_2/mol amine]	0.567	0.567	0.568	0.567	0.567	0.568	0.736	0.735	0.734	0.736	0.736	0.734
CO_2 recovery [%]	90	90	90	90	90	90	90	90	90	90	90	90
CO_2 captured [tonne/h]	73.4	73.4	73.4	73.4	73.4	73.4	73.4	73.4	73.4	73.4	73.4	73.4

a. High pressure fans upstream absorber increase gas temperature by 8 °C

Table 2.6 Gas concentration of AMP + PZ between the absorber section and the water wash using solvent B

CASE [a]	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
Outlet gas pressure [kPa]	103	103	103	103	103	103	103	103	103	103	103	103
Outlet gas flow [kmol/h]	57	57	57	57	57	57	53	53	53	53	53	53
Outlet gas temperature [°C]	55.5	55.6	55.6	55.5	55.5	55.6	44.0	44.1	44.2	43.9	44.0	44.1
Gas concentration of AMP + PZ [ppmv]	**554**	**532**	**512**	**550**	**528**	**509**	**236**	**226**	**217**	**232**	**223**	**214**
Liquid fugacity of solvent B [Pa]	19	18	17	19	18	17	5	5	4	5	5	4
CO_2 content [mol fraction]	.003	.003	.003	.003	.003	.003	.003	.003	.003	.003	.003	.003
Water content [mol fraction]	0.14	0.13	0.13	0.14	0.13	0.13	0.08	0.08	0.08	0.08	0.08	0.08
Inert gas content [mol fraction]	0.86	0.86	0.86	0.86	0.86	0.86	0.92	0.92	0.92	0.92	0.92	0.92
Gas velocity [m/s]	3.07	3.06	3.06	2.04	2.04	2.04	2.77	2.77	2.77	1.85	1.84	1.84
Gas flow [1000 m^3/h]	1510	1510	1500	1510	1510	1500	1360	1360	1360	1360	1360	1360

a. See table 2.5 for the different process conditions used in simulations

2.1.5 Conclusions WP 1a

Simulations using rigorous simulations of an absorber with no water wash show that the losses of solvent A (MEA) is between 155 ppm at an inlet lean loading of 0.15 and temperature of 40 °C and 44 ppm at an inlet lean loading of 0.25 and temperature of 25 °C and otherwise similar operation conditions. Solvent B had in general about 4 times larger losses at the absorber outlet. An analysis of the data shows that a water wash will greatly reduce these losses.

2.2 Droplet and fume formation assessment (WP 1b)

2.2.1 Liquid entrainment

Liquid entrainment of droplets from the beds is a result of carry over from packed sections and trays as well as from liquid distributors with the discharging flue gas. Down flowing liquid is always in contact with up flowing gas in the type of absorber described in chapter 2.1. Liquid entrainment is therefore a normal physical phenomenon in absorber columns.

Ideally the absorbing liquid should stick to the structured packing material forming continuous film counter current with the flue gas. However, there will be spots in the absorption column where liquid is detached from the surface of the packing material normally because of gravity and that the easiest way to flow results in free falling liquid. Most of such liquid will very soon hit another part of the packing material and rejoin the liquid film which sticks to the packing.

Small quantities of free falling liquid will normally form drops. Drop formation also form satellite drops as shown in figure 2.5. [2]

Some of these drops will be entrained in the gas flow. A large fraction of the satellite drops will be collected in the packing material and in the mist eliminator on top of the packing elements. However, a small fraction of these droplets are sufficient small to penetrate through downstream packing elements and demister.

Spots where liquid is detached and drops are formed are between the liquid distributors and the packing elements and also within each packing elements.

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[2] Investigation of Local Absorption rates in Falling-Film Absorption. Sustainable Thermal Systems Laboratory George W. Woodruff School of Mechanical Engineering. Georgia Institute of Technology, Copyright 2009. http://www.me.gatech.edu/stsl/research-falling.html

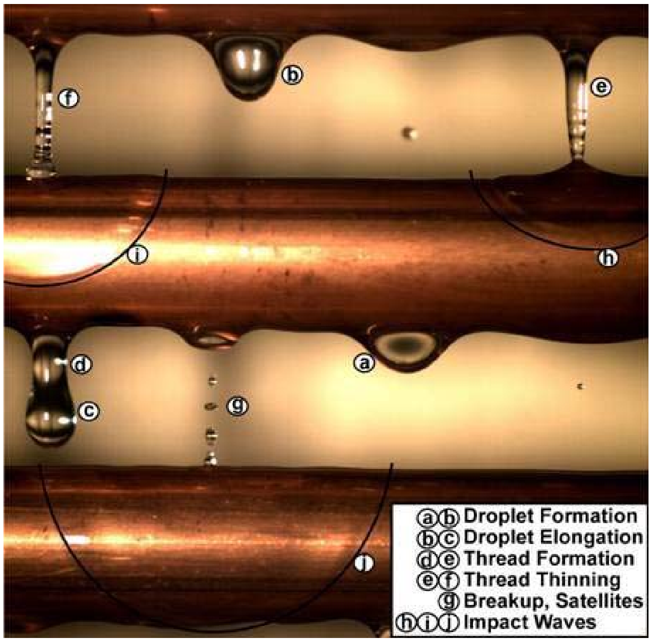

Figure 2.5 Droplet formation from free falling liquid in horizontal tube banks

Small satellite drops will also be formed by collision-induced breakup during droplet/droplet and droplet/surface collisions. The number of small liquid fragments per collision depends on the stability of the liquid surfaces formed during the collision process.

Liu Jing (2010) has performed a numerically study of deformation and breakup of liquid drops in gas flow.[3] His work comprised four typical breakup modes: oscillation, bag breakup, sheet stripping breakup and shear breakup, which occur under different conditions.

The author described a rather complicated breakup mode at a liquid/gas density ratio equal to 1 000. He called it the multimode breakup mode. This mode comprised shear breakup and piercing breakup. He showed different breakup modes in the form of Re_g-We_g breakup map with different density ratios. The gas viscosity and the liquid surface tension are subject to change respectively as Re_g and We_g vary. Figure 2.6 shows the map calculation for the density ratio equal to 1 000.

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[3] Liu Jing:” Direct Numerical Simulation of Secondary Breakup of Liquid Drops” Chinese Journal of Aeronautics 23(2010) 153-161

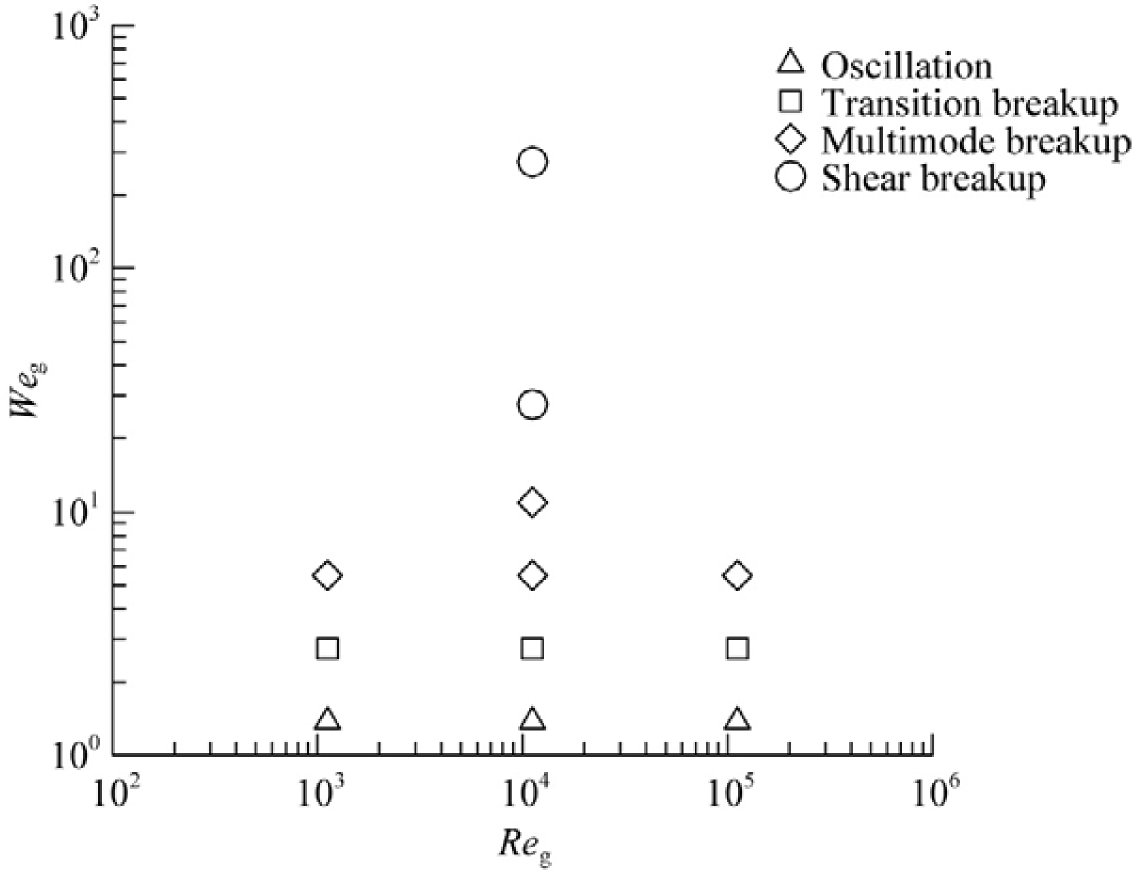

Figure 2.6 Re_g-We_g breakup map (c) γ=1 000

Foaming within the packed sections will result in formation of satellite droplets from liquid film rupture. Such break-up of surface films into fragments of small droplets comprises several successive events governed by physical parameters such as Rayleigh instability, Marangoni forces[4,5], dynamic viscosity, surface elasticity, critical film thickness[6] and gas flow induced shear stress.

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[4] E. A. Chinnov, O. A. Kabov: "Marangoni Effect on Wave Structure in Liquid Films". Microgravity Science and Technology, Volume 19, Numbers 3-4, 18-22, doi: 10.1007/BF02915739

[5] Stergios G. Yiantsios, Brian G. Higgins: "A mechanism of Marangoni instability in evaporating thin liquid films due to soluble surfactant". Phys. Fluids, Vol. 22, Number 2, (2010); doi:10.1063/1.3316785 (12 pages)

[6] J.E. Coonsa, P.J. Halleyb, S.A. McGlashanb and T. Tran-Congc:"Scaling laws for the critical rupture thickness of common thin films". Colloids and Surfaces A: Physicochemical and Engineering Aspects. Volume 263, Issues 1-3, 1 August 2005, Pages 258-266.
A collection of papers presented at the 5th European Conference on Foams, Emulsions, and Applications, EUFOAM 2004, University of Marne-la-Vallee, Champs sur Marne (France), 5-8 July, 2004

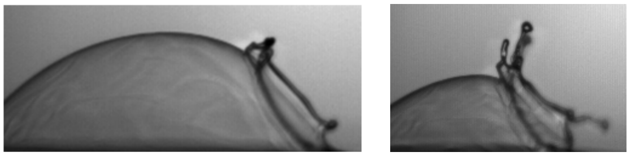
The chain of events can be categorized as follows[7]:

1. Film Thinning
   Liquid draining induces instabilities which generate a wave like non uniformity in bubble film thickness.

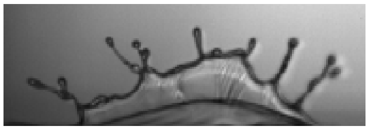
2. Initial Rupture
   Non uniformity in bubble film thickness makes the film reach a critical thickness at a single starting point for the rupture.

3. Hole expansion
   The initial small hole (starting point) widens uniformly in a circular profile. Liquid from the ruptured film accumulates at a rim around the periphery of the hole. The hole broadens collecting more liquid along the rim.

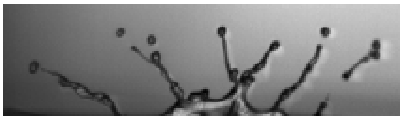
4. Rim reach liquid surface
   The rim loses its uniformity and some velocity.



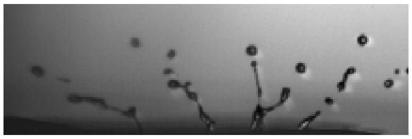
5. Formation of ligaments and thin films
   The rim converts into a toroidal network of crests and troughs. Thicker portions (troughs) form long ligaments and the thinner portion (crests) form thin films connecting the ligaments.



6. Formation of toroid surfaces
   The films disappear forming long toroid surfaces converting into long wavy cylinder shapes.



7. Film drop production
   Toroid surfaces and wavy cylinders undergo surface tension driven break up into several small fragments.
   The fragments form very small drops known as film drops.



The events 4, 5, 6 and 7 are shown in photograph pictures.

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[7] Rainy Shukla: "Experimental Studies on Bubble Rupture Mechanicsm". MSc Thesis 03/04/2009 University of Cincinnati. Mechanical Engineering of the College of Engineering.

Foaming is usually caused by contamination of the solvent amine by degradation products, surface active agents (e.g. corrosion inhibitors), lubricating oil aerosols, finely divided suspended particles, high gas velocity and also excessive antifoam addition. Foaming will result in:

- High amine loss and amine carry-over
- Reduced removal efficiency
- High pressure drop in absorber and/or stripper

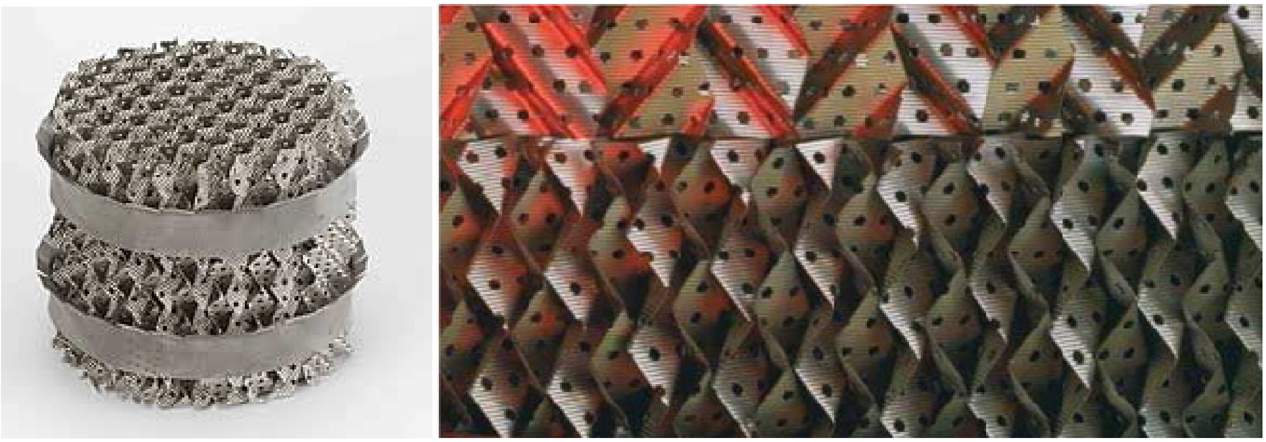
Some measures can be used to prevent or reduce foaming:

- Mechanical and activated carbon filtration of a 10-20% solvent slipstream
- Antifoam addition
- Caustic addition to neutralize HSS

The amount of liquid entrainment is normally a function of gas and liquid load. Increased gas velocity and density results in a larger liquid hold up more shear stress on liquid films which enhance droplet formation. Increased flow of absorbing liquid results increased thickness of liquid films on packing elements and higher real gas velocities, which both enhance entrainment.

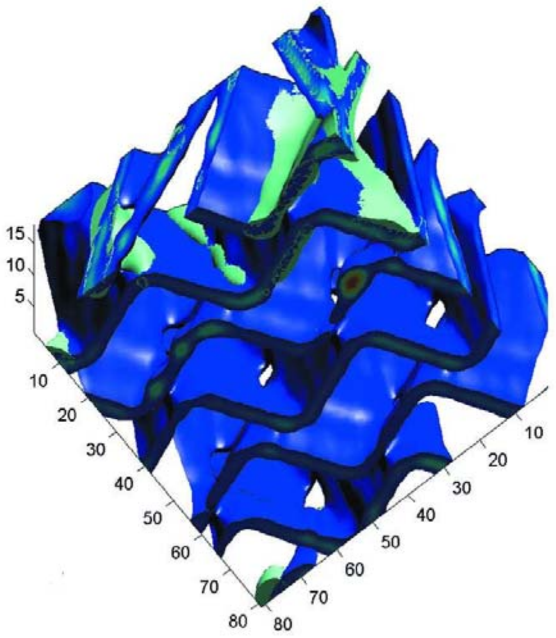
Suppliers of packing elements give guidelines of optimal superficial gas velocities and gas liquid ratios for optimal performance and acceptable entrainment.

Figur 2.7 shows an example of physical shapes of structured packing elements and figure 3.8 shows liquid hold-up illustrated by X-ray tomography.



Left: Mellapak 250.Y/X http://www.sulzerchemtech.com/en/etracker.aspx/raid-71108/tabid-148/gid-Documents.11.2744/
Right: Flexipac http://pdf.directindustry.com/pdf/koch-glitsch/structured-packing/21790-51726-_3.html

Figure 2.7 Example of structured packing elements from Sulzer and Koch-Glitsch



58Figure 2.8 Liquid hold-up in Mellapak packing element illustrated by X-ray tomography[8]

Possible packing could be Flexipac 2X from Koch-Glitsch. Here the wave length of the corrugated plates is typical 25 mm. Each bending has 90 degree angle. The corrugated plates are perforated and produced with a textured surface roughness in order to increase performance and specific surface. Flexipac 2X has a specific surface of 225 m^2/m^3.

The X-type packing have a nominal inclination angle of 60° from horizontal and are used where high capacity and low pressure drop are required. The Y-type packing has a nominal inclination angle of 45º from the horizontal, and are the most widely used.

Gas velocity distribution and local liquid hold-up within the packing elements are important factors that affect formation of liquid films and droplets. Predicting gas velocity distribution by CFD simulations is difficult because of the perforation and textured surface roughness.

Active physical mechanisms which result in droplet formation in the size range of 0.1 – 1 μm is important, because such droplets can not be separated by inertial impaction. If these droplets are formed at different places in the absorption column, the concentration of the sub-micron aerosol will increase towards clean gas outlet.

The concentration of the sub-micron droplet fraction will be much smaller than the concentration of larger drops from the packing elements. The fraction of sub-micron droplets has not been a topic for natural gas cleaning application. However, this fraction should be important if very strict regulation of stack gas emissions applies, like concentration limits of 0.01 – 1 ppm, when ppm means number of moles of a pollutant in both gas phase and dispersed liquid phase relative to the total number of moles of all substances in the gas phase.

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[8] Marchot, P. et al.:"Liquid Distribution Images on Structured Packing by X-Ray Computed Tomography". AIChE Journal, vol. 47, No. 6, June 2001, pp 1471-1476.

2.2.2 Fume (fog) formation

In gas–liquid contact devices like absorbers, scrubbers, quench coolers, or condensers, aerosols can be formed by spontaneous condensation or de-sublimation in supersaturated gas–vapour mixtures.[9]

Super saturation is a necessary precondition of spontaneous phase transitions and aerosol formation. The degree of saturation **S** in a multi component mixture of an inert carrier gas and **K** condensable (vapour) components can be defined by:

$$\mathbf{S} = \frac{p(T, y_1^G, \ldots, y_K^G)}{p_s(T, y_1^G, \ldots, y_K^G)}, \qquad (2.1)$$

Where p is the actual total pressure of all vapour components i (i = 1, ...K + 1, component K + 1 being the inert gas) and p_s the total equilibrium pressure at the dew point of the vapour mixture.

The total pressure p or p_s, respectively, can be calculated as the sum of the individual partial pressures of all condensable components according to Dalton.

Excluding chemical reactions in the gas phase, super saturation (**S**>1) in a gas–liquid contact device can arise if the dew line is crossed by the process trajectory (or process path) which describes the change of state of the gas phase due to simultaneous heat and mass transfer between both phases. The saturation **S** has to exceed a critical barrier before nucleation and consequently aerosol formation can take place. Two nucleation mechanisms can be distinguished.

Homogeneous nucleation occurs if critical molecule clusters, so-called nuclei, are formed only by molecules of condensable components. This mechanism requires a high degree of critical saturation S_{crit}.

If gas-borne fine particles are present, aerosol formation can be initiated by heterogeneous nucleation, which requires only a very small critical super saturation close to unity. Heterogeneous nucleation is the dominant mechanism of aerosol formation in most industrial gas cleaning processes, because there is normally a large concentration by number of nano-particles in such gases. After nucleation, the aerosol droplets grow by condensation until the super saturation of the gas phase disappears.

Fog formation is most noticeable in the condensation of sulphuric acid and also certain organic vapours in the presence of an inert gas.

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[9] Ehrig, R., Ofenloch, O., Schaber, K., Deuflhard, P.: "Modelling and simulation of aerosol formation by heterogeneous nucleation in gas–liquid contact devices". Chemical Engineering Science **57**(2002) 1151–1163

The formation of fog in a cooler-condenser depends on the relative rates of decrease of temperature and concentration of condensing components.[10]

The risk of fog formation from a condensing vapour component increases when the thermal diffusivity in the gas mixture, $D_{TM} = k/(c_p\rho)$, becomes larger than the diffusion coefficient, D_{VG}, of the vapour component:

$D_{TM}\ (m^2\ s^{-1}) > D_{VG}\ (m^2\ s^{-1})$

k = thermal conductivity of the vapour gas mixture ($W\ m^{-2}K^{-1}$)
c_p = specific heat of the vapour gas mixture ($J\ kg^{-1}\ K^{-1}$)
ρ = density of the vapour gas mixture ($kg\ m^{-3}$)

This condition corresponds to: $\mathbf{Le = Sc/Pr = k/(c_p\rho D_{VG}) > 1}$ (2.2)

Le = Lewis number
Sc = Schmidt number = $\mu/(\rho D_{VG})$
Pr = Prandtl number = $(\mu c_p/k)$

Fog formation will create submicron droplets which penetrate washing units and demisters.

Figure 2.9 shows cooling situations where fog formation occurs.[11]

From a thermodynamic point of view, fog formation may occur if a condition of super saturation exists at any point in the gas. This will happen whenever heat is removed from the gas at a rate compared to the rate of mass transfer sufficient to cause the temperature to fall below the dew point.

Risk of fog formation might occur at the top of the absorber column, where saturated gas heated from exothermal absorption reactions meets cool, lean solvent. According to figure 3.3 the temperature difference between gas and solvent at top of the absorber can reach 15 – 20 °C. There is also a risk of fog formation around liquid distributors and in the cooling water wash sections further up.

Fog formation depends very much on the presence of condensation nuclei. Some condensers might suddenly begin to produce fog without any noticeable change in operating conditions. This may continue for several days after which the fog gradually disappears. Such situations are most likely related to variations in fog nuclei concentrations formed from impurities present in the gas.

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[10] H. F. Johnstone, Max D. Kelley, D. L. McKinley:" Fog Formation in Cooler-Condensers", Ind. Eng. Chem., 1950, 42 (11), 2298–2302

[11] S. Kaufmann, Y. Loretz and K. Hilfiker:"Prevention of fog in a condenser by simultaneous heating and cooling." Heat and Mass Transfer, Volume 32, Number 6, (1997), 403-410.

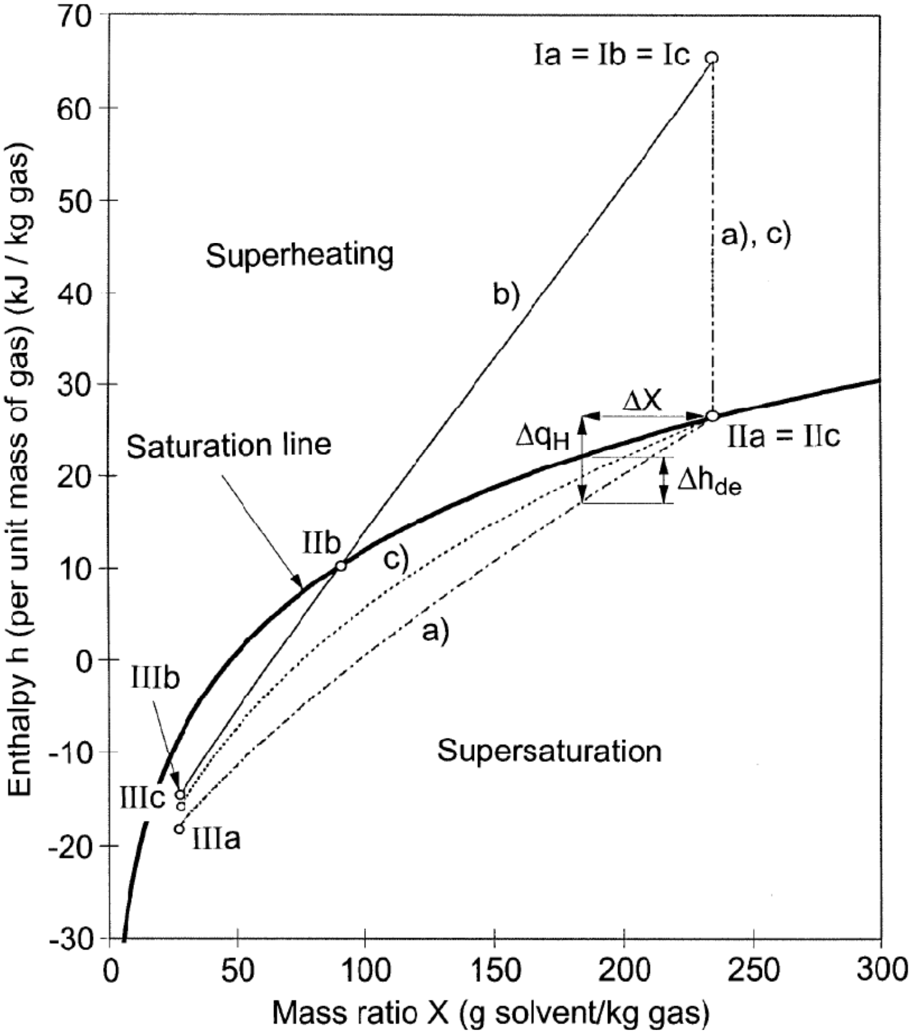

Figure 2.9 Enthalpy versus mass ratio diagram with calculated process lines for bulk flow in different cooling situations

a. Idealized pre-cooling of superheated mixture from Ia to IIa and condensation with supersaturation from IIa to IIIa

b. Condensation of superheated mixture from from Ib to IIb and condensation with supersaturation from IIb to IIIb

c. Like a, but with smaller temperature difference between the bulk flow and the coolant

Liquid water content of fog (LWC) is typical 50 mg/Nm^3 dry air. If such a concentration of liquid aerosol also appear in gas outlet from the absorption column containing 12 vol. % water vapour and the droplets contain 10 wt % of MEA, then the corresponding concentration of liquid MEA in the gas becomes:

$50\cdot(10/100) = 5$ mg/Nm^3 dry air $= 5\cdot[(100-12)/100]\cdot 22.414/61.08 = 1.6$ ppm

Molecular weigt of MEA = 61.08   Molecular volume = 22.414 Nm^3/kmol

See foot note in chapter 1.2 about conversion from mg/Nm^3 dry air to ppm.

Fog formation and outlet concentration of dispersed droplets depends very much on process conditions. Reliable droplet concentration levels and amine content in such droplets should be demonstrated by pertinent and thoroughly performed laboratory and pilot experiments.

2.3 MEA degradation products VLE assessment (WP 1c)

Physical data on degradation products and their volatility are given in an excel spread sheet in appendix 4 submitted together with this report.

The spread sheet gives information on likely degradation products from the solvent MEA, MDEA, AMP and Piperazine and references to observations of the components in the CO_2 capture literature (if they have been observed experimentally).

The data given in the spread sheets are also summarized in table 2.7, table 2.8 and table 2.9. These tables do however contain less information than the spread sheet.

In the tables are given simple estimates of emissions of different degradation products. It should be emphasized that these represent informed guesswork. To our knowledge, there are no broad quantitative studies in open literature on the formation of degradation products in post-combustion CO_2 capture plants. The available data also comes from different CO_2 capture plants and different lab-scale experiments. Great caution should be used when comparing data on solvent degradation obtained under different degradation conditions.

The numbers given are also mostly conservative (high). The sum of the degradation products in the tables would imply a higher level of overall solvent degradation than is usually allowed in CO_2 capture plants.

The estimates of emissions are based on a few simple assumptions. For volatile degradation product emissions are assumed to be proportional to the rate of formation. The rate of formation is given as a fraction of the ammonia emission number. The underlying assumption is that ammonia formation is an indicator of the overall degradation rate in the plant and that volatile degradation products do not accumulate in the plant. This is probably a reasonable model assumption, but probably not equally valid for all degradation products. It is for example not valid for nitrosamines that may be formed in reaction with secondary amine solvents.

For table 2.7 calculations we have assumed an ammonia concentration emission level of 1 ppm for MEA, 0.5 ppm for MDEA, and 0.05 ppm for AMP and Piperazine. This is based on a simple estimate of the relative stability of the solvents.

For medium volatility degradation products vapour emissions are assumed to be proportional to volatility and concentration in the liquid. The concentrations in the liquid are based on informed guesswork.

In table 2.7 are listed volatile degradation products. These are defined as any component having a free energy of solvation higher than -5 kcal/mol.

In table 2.8 are listed medium volatility degradation products. Medium volatility degradation products are defined as a component having a free energy of solvation (dG solv) < -5 kcal/mol and that are not on ionic form.

In table 2.9 are listed non-volatile degradation products. These are defined as compounds that are expected to be on ionic form in post-combustion CO_2 capture plant.

In a conventional post-combustion CO_2 capture power plant volatile degradation products probably presents the greatest challenge in terms of emissions, since it is difficult to keep such components from escaping the plant with a conventional water wash.

Nitrosamines and nitramines are marked with red in the tables. These compounds probably present the greatest health and environmental risk among the emitted compounds.

We have in this work considered the degradation of each solvent component separately. In a solvent system with two components, there will most likely be formed other degradation products in addition to those formed by the solvents in single component systems. We do however not believe that such additional degradation products would significantly change the emission profile of the solvent system. There are also very few studies in open literature looking at degradation in mixed solvent systems.

Maximum exit concentration level of N-nitrosodiethanolamine* is calculated below as an example of how to use the tables.

This compound is a medium volatility degradation product and appears at the third page of table 2.8. If the emission concentration level of MEA is 1 ppm then the maximum emission level of N-nitrosodiethanolamine becomes 0.5 ppb. If the emission level of MEA is 0.2 ppm then the maximum emisson concentration level of N-nitrosodiethanolamine becomes 0.1 ppb.

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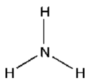
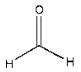
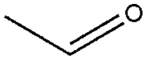
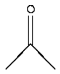
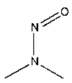
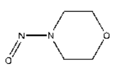
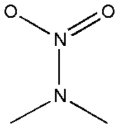
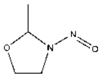
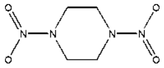
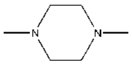
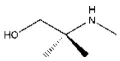
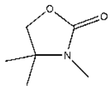
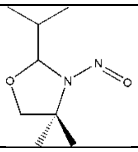
*N-Nitrosodiethanolamine is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity in experimental animals

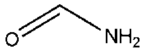
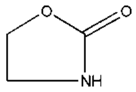
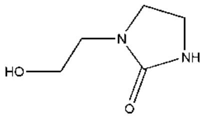
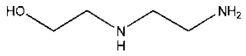
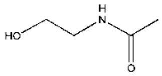
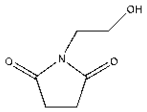
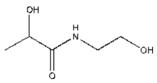
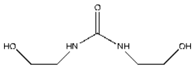
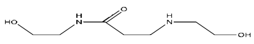
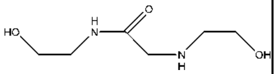
Table 2.7 Volatile degradation products

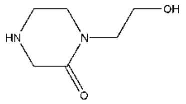
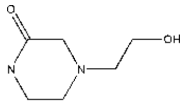
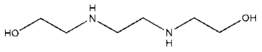
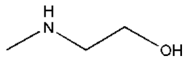
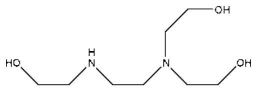
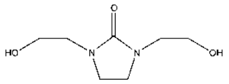
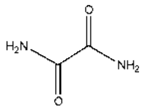
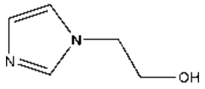
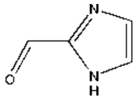
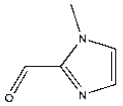
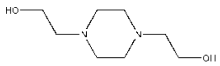
Degradation product	CAS.	Structure	Emission[a] [ppm]	Ref./Comment
Ammonia	7664-41-7		1 (MEA) 0.05 (Pip) 0.5 (MD) 0.05 (AMP)	Oxidative degradation product, expected for all solvents.
Methylamine	74-89-5	H_2N—	0.006 (MEA) $3*10^{-4}$ (Pip) 0.03 (MD) $3*10^{-4}$ (AMP)	May form from oxidative degradation.
Formaldehyde	50-00-0		0.08 (MEA) 0.004 (Pip) 0.004 (MD) 0.004 (AMP)	
Acetaldehyde	75-07-0		0.02 (MEA) 0.001 (Pip) 0.009 (MD) 0.001 (AMP)	
Acetone	67-64-1		0.002 (MEA)	
dimethylamine	124-40-3		0.01 (MEA) $5*10^{-5}$ (Pip) $5*10^{-4}$ (MD) $5*10^{-5}$ (AMP)	
ethylamine	75-04-7		0.01 (MEA) $3.5*10^{-5}$ (Pip) $3.5*10^{-4}$ (MD) $3.5*10^{-5}$ (AMP)	
diethylamine	109-89-7		0.01 (MEA) $7*10^{-5}$ (Pip) $7*10^{-4}$ (MD) $7*10^{-5}$ (AMP)	
N-nitrosodimethylamine	62-75-9		0.02 (MEA) 0.001 (Pip) 0.01 (MD) 0.001 (AMP)	
4-nitroso-morpholine	59-89-2		0.01 (MEA) $4*10^{-4}$ (MD)	

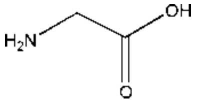
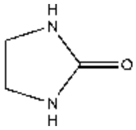
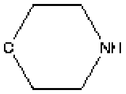
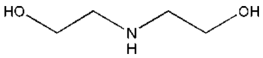
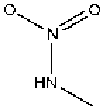
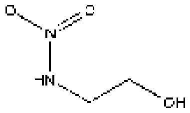
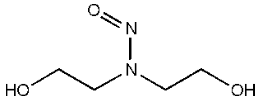
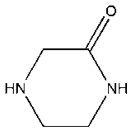
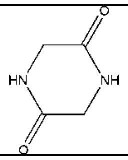
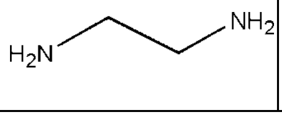
Dimethylnitramine	4164-28-7		0.02 (MEA) $1*10^{-4}$ (Pip) 0.001 (MD) $1*10^{-4}$ (AMP)	
2-methyl-3-nitroso-oxazolidine	39884-53-2		0.003 (MEA)	Degradation product suggested by R. Loeppky
1,4 dinitropiperazine	140-79-4		$1*10^{-4}$ (Pip)	
1,4 dimethylpiperazine	106-58-1		0.004 (MD)	
2-methyl-2-(methylamino)- 1-Propanol	27646-80-6		$3*10^{-4}$ (AMP)	Degradation product observed in the work of H. Lepaumier.
3,4,4-trimethyl oxazolidin-2-one	15833-17-7		$5*10^{-4}$ (AMP)	Degradation product observed in the work of H. Lepaumier.
4,4 dimethyl-2-isopropyl-3-nitrosooxazolidine	39884-58-7		0.015 (AMP)	

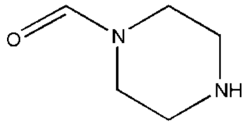
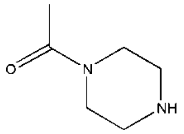
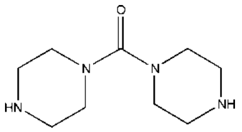
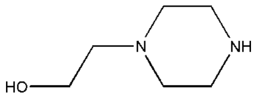
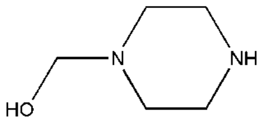
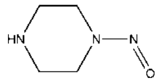
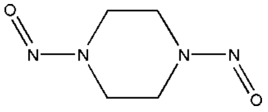
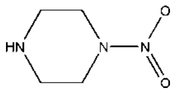
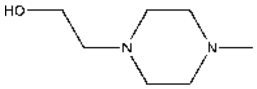
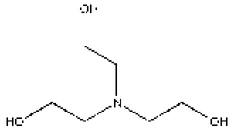
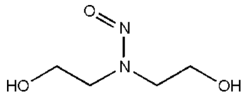
a: MD is short for MDEA, N-methyl diethanolamine

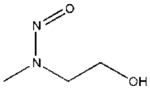
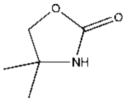
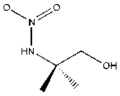
Table 2.8 Medium volatility degradation products

Degradation product	CAS.	Structure	Emission[a] [ppm]	Ref./Comment
Formamide			0.007 (MEA) 0.003 (Pip) 0.006 (MD) 0.003 (AMP)	
Oxazolidin-2-one			0.004 (MEA)	
1-(2_hydroxyethyl)-2-imidazolidinone	3699-54-5		0.003 (MEA)	
N-(2-hydroxyethyl)-ethylenediamine	111-41-1		0.003 (MEA)	
N-(2-hydroxyethyl)-acetamide/N-acetylethanolamine	142-26-7		0.003 (MEA)	
1-(2-hydroxyethyl)-2,5-Pyrrolidinone	18190-44-8		0.003 (MEA)	
N-(2-Hydroxyethyl)lactamide	5422-34-4		0.003 (MEA)	
N,N-di(2-hydroxyethyl)urea	15438-70-7		0.003 (MEA)	
N-(2-hydroxyethyl)-3-[(2-hydroxyethyl)amino]-Propanamide	587876-41-3		0.003 (MEA)	
N-(2-hydroxyethyl)-2-[(hydroxyethyl)amino]-acetamide	144236-39-5		0.003 (MEA)	

1-(2-hydroxyethyl)-2-piperazinone	59702-23-7		0.003 (MEA)	
4-(2-hydroxyethyl)-2-piperazinone	23936-04-1		0.003 (MEA)	
2-((2-[(2-hydroxyethyl)amino]ethyl)amino)ethanol	4439-20-7		0.003 (MEA)	
2-methylaminoethanol	109-83-1		0.01 (MEA)	
2,2'-[[2-[(2-hydroxyethyl)amino]ethyl]imino]bis-Ethanol	60487-26-5		0.003 (MEA)	
1,3-bis(2-hydroxyethyl)-2-Imidazolidinone	71298-49-2		0.003 (MEA)	
Oxalamide	471-46-5		0.003 (MEA)	
1-(2-Hydroxyethyl)imidazole	1615-14-1		0.03 (MEA)	
1H-imidazole-2-carboxaldehyde	10111-08-7		0.003 (MEA)	
1-methyl-1H-imidazole-2-carboxaldehyde	13750-81-7		0.003 (MEA)	
N,N-bis(hydroxyethyl)piperazine	122-96-3		0.003 (MEA)	

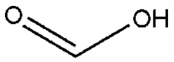
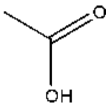
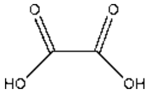
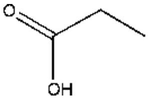
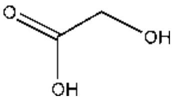
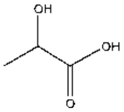
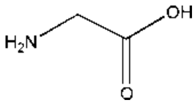
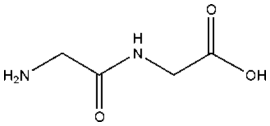
Glycine	56-40-6		0.003 (MEA)	
Hydroxy-Acetaldehyde	141-46-8		0.003 (MEA)	
2-imidazolidinone	120-93-4		0.003 (MEA)	
morpholine	119-91-8		0.02 (MEA)	
diethanolamine	111-42-2		0.003 (MEA)	
methylnitramine	598-57-2		0.02 (MEA) 0.002 (Pip)	
2-(nitroamino) ethanol	74386-82-6		0.006 (MEA)	Not known to what extent nitramines may form in CO_2 capture plants
N-nitroso diethanolamine	1116-54-7		0.0005 (MEA) 0.001 (MD)	Nitrosamines have been detected in CO_2 capture plants.
2-oxopiperazine	5625-67-2		0.002 (Pip)	Possible oxidative degradation product
2,5-piperazinedione	106-57-0		0.002 (Pip)	Possible oxidative degradation product
Ethylenediamine	107-15-3		0.002 (Pip)	

1-Piperazinecarboxaldehyde	7755-92-2		0.003 (Pip)	
1-Acetylpiperazine	13889-98-0		0.003 (Pip)	
1,1'-carbonylbis piperazine	17159-16-9		0.002 (Pip)	
1-Piperazineethanol	103-76-4		0.005 (Pip)	
N-(hydroxymethyl)piperazine	90324-69-9		0.002 (Pip)	
1-nitrosopiperazine	5632-47-3		0.002 (Pip)	Possible nitrosamine degradation product
1,4 dinitrosopiperazine	140-79-4		0.2 (Pip)	Possible nitrosamine degradation product
1-nitropiperazine	42499-41-2		0.003 (Pip)	Possible nitramine degradation product
4-methyl-1-Piperazineethanol	5464-12-0		0.2 (MD)	Observed experimentally
triethanolamine	102-71-6		0.006 (MD)	
N-nitroso ditethanolamine	1116-54-7		$8*10^{-4}$ (MD)	

2-(methylnitrosoamino) ethanol	26921-68-6		0.3 (MD)	
4,4-dimethyl-2-Oxazolidinone	26654-39-7		0.01 (AMP)	
nitro 2-amino-2-methylpropanol	no cas		$3*10^{-4}$ (AMP)	

a: MD is short for MDEA, N-methyl diethanolamine

Table 2.9 Non volatile degradation products

Degradation product	CAS.	Structure	Emission[a] [ppm]	Ref./Comment
Formic acid/formate	64-18-6		0.003 (MEA) 0.002 (Pip) 0.003 (MD) 0.002 (AMP)	Known oxidative degradation product
Acetic acid/acetate	64-19-7		0.03 (MEA) 0.002 (Pip) 0.003 (MD) 0.002 (AMP)	Known oxidative degradation product
Oxalic acid	144-62-7		0.003 (MEA) 0.002 (Pip) 0.003 (MD) 0.002 (AMP)	Known oxidative degradation product
Propanoic acid/Propinoic acid	79-09-4		$3*10^{-3}$ (MEA)	
Hydroxy-acetic acid/glocolate/glycolic acid	79-14-1		$3*10^{-3}$ (MEA)	
Lactic acid/Lactate	598-82-3		$3*10^{-3}$ (MEA)	
Glycine	56-40-6		$3*10^{-3}$ (MEA)	Possible oxidative degradation product
N-Glycylglycine	556-50-3		$2*10^{-3}$ (Pip)	Likely oxidative degradation product

a: MD is short for MDEA, N-methyl diethanolamine

3. EMISSION-REDUCING TECHNOLOGY (ERT) IDENTIFICATION

3.1 Water wash system assessment (WP 2a)

3.1.1 A general comment regarding the simulation work of the water wash

We have from the simulations seen that one might not approach phase equilibrium at the top output of the column. There are uncertainties as to the gas film resistance model used in CO2SIM. We are using a Reynolds analogy model, which as not been specifically validated towards pilot plant data. From the equilibrium based models, it is shown that there are still driving forces at the outlet, as shown with the parallel work performed with the simplified f factor model. It is not know which model is the correct one and from this we might therefore say that the simulation results from CO2SIM are conservative, with larger simulated emissions compared to the f-factor model. More work should be done to verify the extent of gas film resistance.

3.1.2 Water-wash section

A water section on top of the absorber is the state of the art method to minimize solvent losses from the leaving gas and keeping the amine emissions to the air as low as possible.

In a water-wash section the amine in the gas from the absorber outlet is absorbed by water coming from the top of the water-wash section. The water/amine liquid is subsequently brought back into the process liquid system.

However, the water balance of the system does not allow substantial amount of fresh water to be used because any excess water coming into the liquid system must be removed in the desorber unit by evaporation which is not energy efficient. In fact, it is very important that the amount of water leaving the absorber wash section with the flue gas is close to equal to the amount of water coming into the absorber with the flue gas. This water balance has only to take into consideration the small amount of water (approx 1%) leaving with the product CO_2 stream.

Since the packing needs a minimum liquid flow in order to provide wetted surface and good contact between gas and liquid, the water is recycled several times in the section and the fresh water is only a fraction of the total liquid flow in the water wash. A corresponding bleed stream normally enters the absorber together with the lean liquid feed. The recycling of liquid also implies that counter current effect is small because the amine concentrations is almost the same in the top and the bottom of the section and maximum one single amine/water equilibrium stage is attainable.

Therefore, more stages may be obtained by using several water wash sections. In figure 3.1 a two sections water wash configuration is illustrated. Pure make up water is added to the upper section and a bleed from this section is used as make up in the lower section.

In stead of added make up water one may condense water by cooling down the gas inside the water wash section. The cooling is provided by heat exchangers in the re-circulation loop (See figure 3.1). Cooling down the gas is generally favourable because the amine solubility in the water increases. Often a combination is used, and for a certain gas temperature it is the total bleed out of the section that keeps the amine concentration down and makes the necessary driving forces for amine solubility.

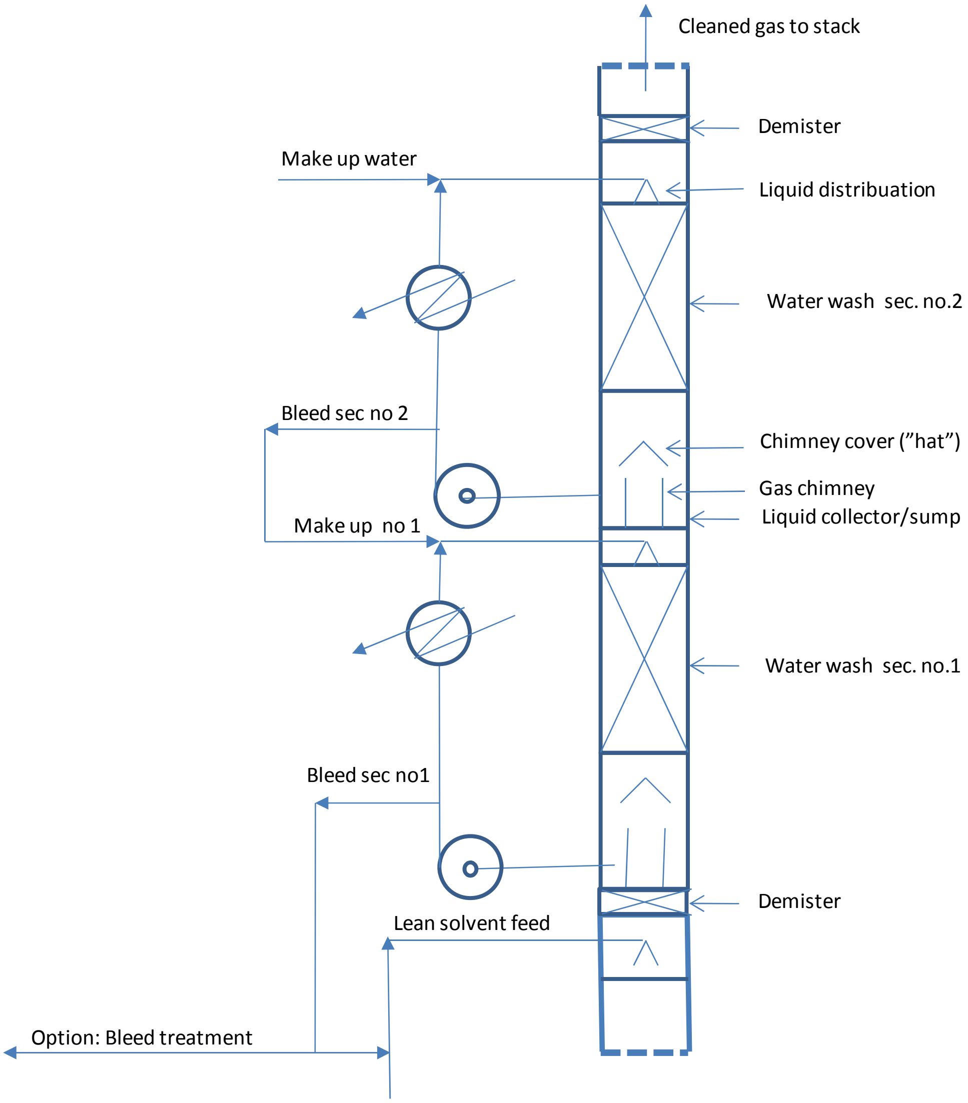


Figure 3.1 Two sections water wash configuration

In order to design a water wash unit several factors should be considered:

1. **Volatility:**
   With increasing volatility of an amine there is a need for the water wash process to be more efficient. Most amine solvents are hydrophilic in character and have a low vapour pressure over an aqueous solution. The vapour pressure is given by the following equation

   $$p_{\mathrm{Am}} = \gamma_{\mathrm{Am}} P^{\mathrm{o}}_{\mathrm{Am}} \, x_{\mathrm{Am\_free}} \qquad (3.1)$$

   Here $P^{\mathrm{o}}_{\mathrm{Am}}$ is the vapour pressure of pure amine, $x_{\mathrm{Am\_free}}$ the mole fraction of amine in the water in free form, i.e. not reacted with CO_2 or in ionized form, and γ is the activity coefficient. The activity coefficient of a component in a solution depends on both its composition and temperature. Figure 3.2 shows how the activity coefficients of MEA water vary with different MEA concentrations and temperatures. For a dilute MEA solution, the activity coefficient of MEA is approximately 0.2 at 40 °C and increases to about 0.4 at 100°C. At a constant temperature, higher concentrations of MEA result in higher activity coefficients. The vapour pressure depends on the concentration of free amine. Formation of carbamate or protonation of the amine will therefore reduce the amine volatility.

2. **Make-up water:**
   It is important to maintain a low concentration of solvent in the circulating water in order to keep the driving force high. The higher the concentration of the solvent, the higher the partial pressure of the solvent and, consequently, the higher the solvent loses. Therefore, relatively clean water must be fed to the water-wash section as make-up while an equal amount of solvent laden water is drawn out. The make-up water source can be condensed water inside the water wash section, condensed water from the stripper section or excess water from the water Direct Contact Cooler (DCC).

3. **Temperature:**
   In general, the solubility of a gas increases as the temperature decreases. Therefore, lowering the temperature of the absorber top and wash water, results in more amine being absorbed.

4. **Number of stages:**
   The greater the number of water wash sections in the process, the lower becomes the concentration of amine in the purified gas stream.

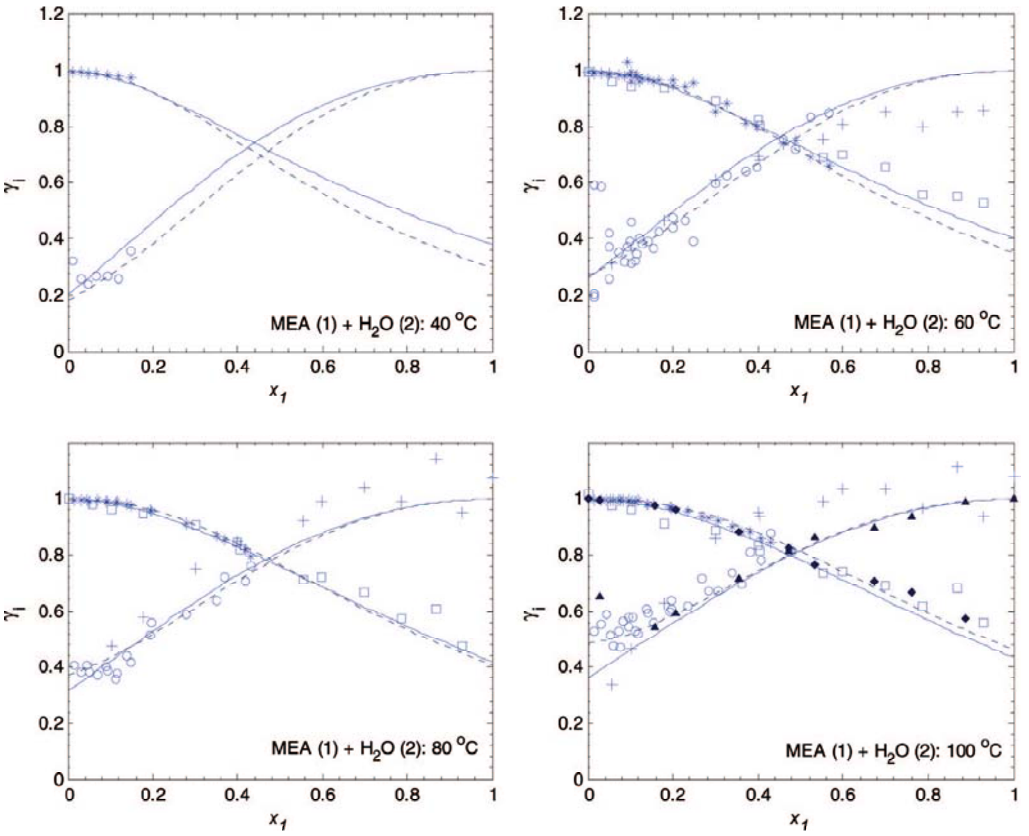


Figure 3.2 Activity coefficients of MEA (γ_1) and water (γ_2), depending on composition at different temperatures: ○, MEA; *, H_2O; solid lines, calculated using Wilson model; dashed lines, calculated using NRTL model (reproduced from Kim et al. *J.Chem.Eng Data* 2008, 53, 2521-2531, [28])

The vapor pressure of a pure component can be predicted by use of an empirical equation as follows:

$$\ln P^{\mathrm{o}}_{\mathrm{Am}} = b_1 + b_2/T + b_3\ln(T) + b_4T^{b_5} \tag{3.2}$$

where $P^{\mathrm{o}}_{\mathrm{Am}}$ is gas pressure in Pa and T is gas temperature in °K. Table 3.1 and figure 3.3 shows parameters *b* for some amines and the relationship between ln P^{o} vs 1/T, respectively.

In spite of the vapour pressures in figure 3.3, AMP is much more difficult to capture in a water wash compared to piperazine even if the vapour pressure for the pure components is lower The reasons are large difference in activity coefficient and loading. The same is even more the case when comparing AMP to MEA.

Dissolved in water AMP is more volatile than MEA, because of the large solubility of MEA in water compared to AMP. In addition MEA vapour from solvent A is more easily absorbed with CO_2 in water compared to the AMP vapour from solvent B. These two favourable characteristics of solvent A give lower amine emission from the CO_2 absorber and as shown in chapter 3.1.5 also better separation efficiency by the water wash sections.

Table 3.1 Vapor Pressure Parameters of some Amine Obtained from DIPPR Database

Component	b_1	b_2	b_3	b_4	b_5	Error, %	$P^{o}_{40\,^{\circ}C}$, Pa
MEA	92.624	-10367	-9.4699	1.9×10^{-18}	6	< 10	164.0
Piperazine	70.503	-7914.5	-6.6461	5.2106×10^{-18}	6	< 5	1143
MDEA	253.07	-18378	-33.972	2.3348×10^{-5}	2	< 10	4.245
DEA	106.38	-13714	-11.06	3.2645×10^{-18}	6	< 5	0.379
AMP [11]	$P^{o}_{Am} = 1\times10^{3}\exp\left(15.155 - \frac{3472.6}{(T-107.32)}\right)$ [12]						179.7

[11] Pappa (2006)

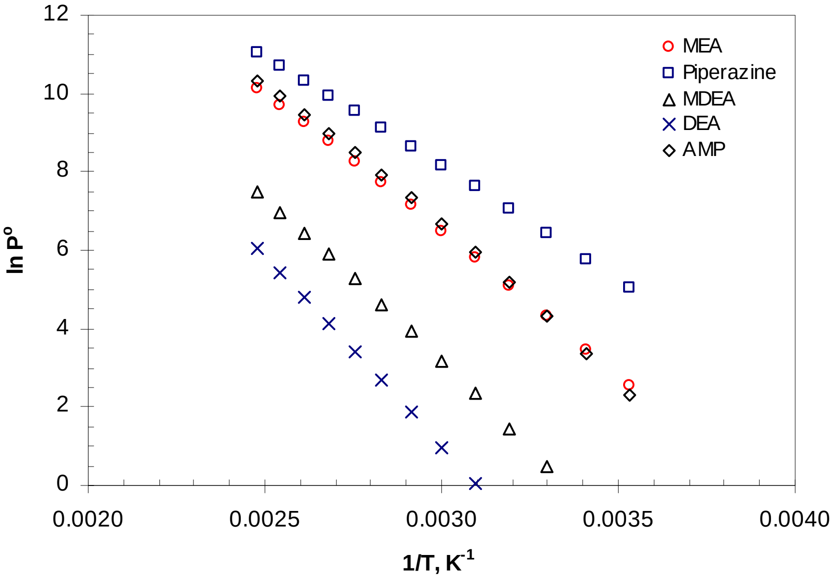


Figure 3.3 Relationship between ln P° vs 1/T for some pure amines

3.1.3 Water balance and waste water

The water sources in the water wash section of CO_2 capture plants are water contained in the flue gas and de-mineralized process water used as make-up water. The water content of the flue gas depends on the properties of the gas and its temperature and pressure. This implies that the flue gas represents a main source of water, whereas the cleaned gas and the CO_2 stream represent the main sinks.

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[12] Georgia D. Pappa, Christos Anastasi and Epaminondas C. Voutsas:" Measurement and thermodynamic modeling of the phase equilibrium of aqueous 2-amino-2-methyl-1-propanol solutions." Fluid Phase Equilibria. Volume 243, Issues 1-2, 10 May 2006, Pages 193-197

The amount of wash water might be given as a mol % of dry inert gas (N_2+O_2+Ar) flow in the flue gas and is given as a parameter β. In the top of desorber the amount of water is about the same as the CO_2 stream (if the plant is optimized). This will give a source of water around 3-4 mol % of inert gas flow for natural gas exhaust case and 10-12 mol % for a coal based exhaust.

The dew point of coal based flue gas from a flue gas desulfurization unit (FGD) is typically 60 °C. The outlet gas from the FGD unit is normally cooled in a direct contact cooler (DCC) by a circulating water stream. By lowering the gas temperature in this way, some of the water contained in the flue gas will condense. This DCC excess water contains little dissolved CO_2 and is sent to a cooling tower, for waste water treatment or to be used as make-up water for water-wash section.

The dew point of flue gas from natural gas combustion is typically 43 °C. Even here a DCC may be used in order to cool the flue gas inlet to the absorber. This cooling makes a temperature reduction in the lower part of the absorber.

The amount of water available for water wash should be about 4-6 mol% of inert gas (β) for the natural gas case. For the coal case one usually has more water available.

A schematic of the water balance in a CO_2 capture plant is shown in figure 3.4.

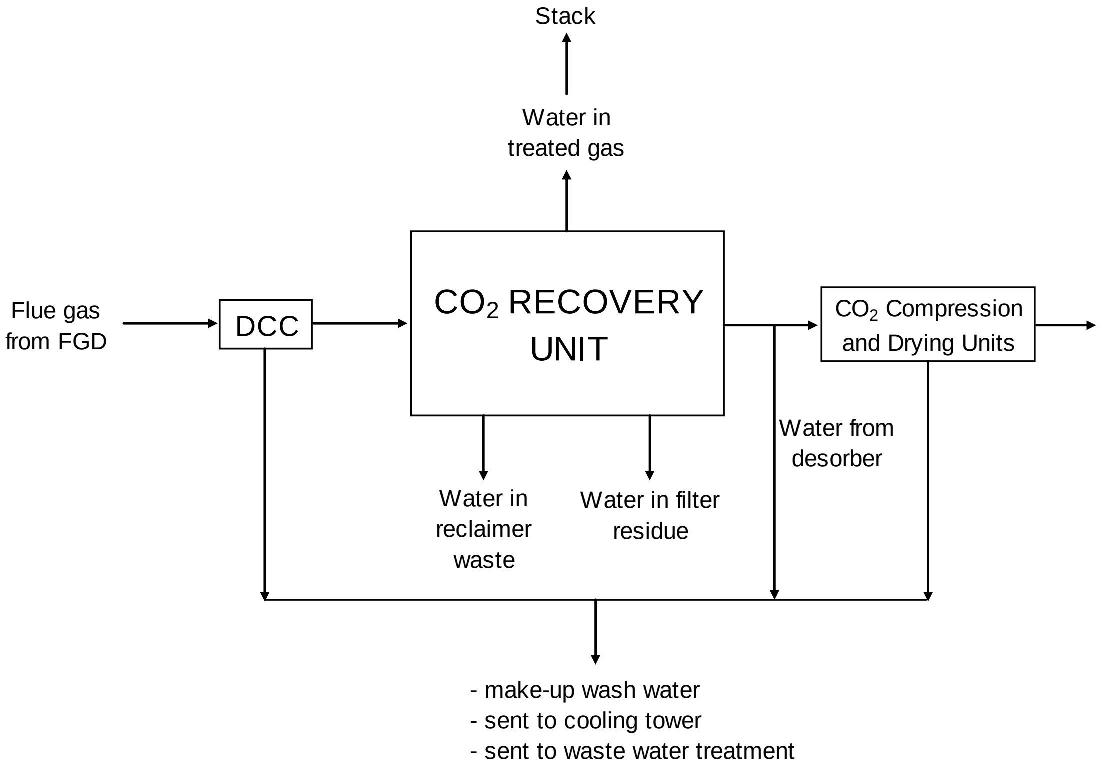


Figure 3.4 Water balance scheme in a CO_2 capture plant

3.1.4 CO2SIM Simulation of absorber with two wash sections

To see the effect of a two stage water wash section with respect to amine slippage, rigorous simulations were performed with CO2SIM for the given case AA1. (See table 2.4)

Case definition

The flow sheet is shown below:

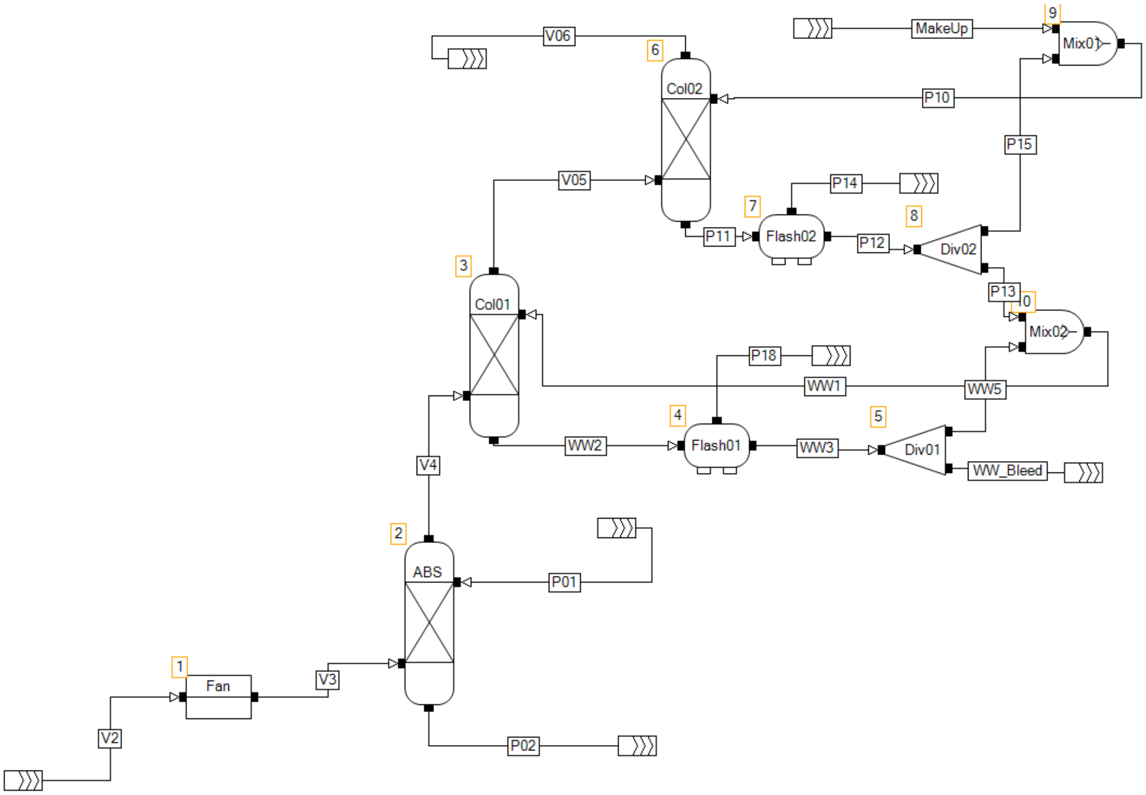


Figure 3.5 Flow-sheet of the modelled process

The basis for the simulations is the following:

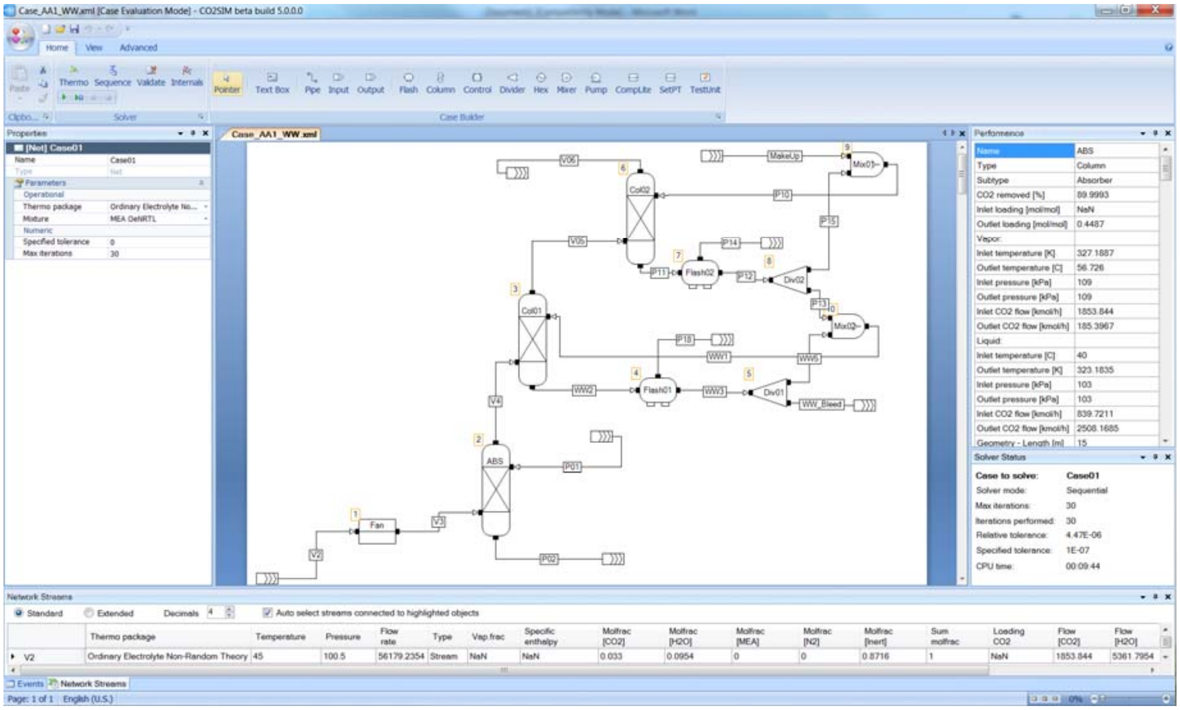
- The ordinary electrolyte non-random theory model (o-eNRTL) is used for describing VLE (similar model as in ASPEN)
- Absorber is set to 90 % CO_2 capture
- Two water wash sections is used as shown in figure 3.5
- Each water wash section contains 2 meter hight of Mellapak 250.Y structured packing from Sulzer Chemtech

Experience from pilot lab tests (water wash using almost isothermal conditions) combined with simulations at SINTEF indicates that the separation efficiency relative to the maximum efficiency at equilibrium condition, $\eta_{eq.\ rel.}$, reaches 90 % after about 1.0 m of packing, and 99 % after 1.5 m of packing.* This may differ from one case to another, but was the reason why a 2 m packing have been used as a standard for one section of water wash at our labs. Standard HETP (Height Equivalent to a Theoretical Plate) for these types of packing is typically less than one meter (approximately 0.7m), which also indicates that 2 meter should be sufficient.

* $\eta_{eq.\ rel} = 100 \cdot (p_{in} - p_{out})/(p_{in} - p_{eq})$

Specific simulation details:

- 36.030 kg/h of water was added in the makeup stream (36 m3/h)
- The recycling wash water in both wash sections where sett to a cooling temp of 30 °C.
- All other details of the simulations can be found in table 3.1.



[Not] Case01	
Name	Case01
Type	Net
Parameters	
Operational	
Thermo package	Ordinary Electrolyte No...
Mixture	MEA OeNRTL
Numeric	
Specified tolerance	0
Max iterations	30

Name	ABS
Type	Column
Subtype	Absorber
CO2 removed [%]	89.9993
Inlet loading [mol/mol]	NaN
Outlet loading [mol/mol]	0.4487
Vapor:	
Inlet temperature [K]	327.1887
Outlet temperature [C]	56.726
Inlet pressure [kPa]	109
Outlet pressure [kPa]	109
Inlet CO2 flow [kmol/h]	1853.844
Outlet CO2 flow [kmol/h]	185.3967
Liquid:	
Inlet temperature [C]	40
Outlet temperature [K]	323.1835
Inlet pressure [kPa]	103
Outlet pressure [kPa]	103
Inlet CO2 flow [kmol/h]	839.7211
Outlet CO2 flow [kmol/h]	2508.1685
Geometry - Length [m]	15

Case to solve: **Case01**
Solver mode: Sequential
Max iterations: 30
Iterations performed: 30
Relative tolerance: 4.47E-06
Specified tolerance: 1E-07
CPU time: 00:09:44

● Standard ○ Extended Decimals 4 ☑ Auto select streams connected to highlighted objects

	Thermo package	Temperature	Pressure	Flow rate	Type	Vap frac	Specific enthalpy	Molfrac [CO2]	Molfrac [H2O]	Molfrac [MEA]	Molfrac [N2]	Molfrac [Inert]	Sum molfrac	Loading CO2	Flow [CO2]	Flow [H2O]
V2	Ordinary Electrolyte Non-Random Theory	45	100.5	56179.2354	Stream	NaN	NaN	0.033	0.0954	0	0	0.8716	1	NaN	1853.844	5361.7954

Figure 3.6 Screen copy of the converged simulation, at 90 % capture

3.1.5 Results

Amine slippage, water condensation and make-up water
From the numbers below, it is shown that, the outlet MEA slippage from the absorber is 155 ppmv, whereas after two stages the slippage is reduced to below 1 ppmv.

Outlet stream	MEA slippage (ppmv)
V4	155.5
V05	9.5
V06	0.6

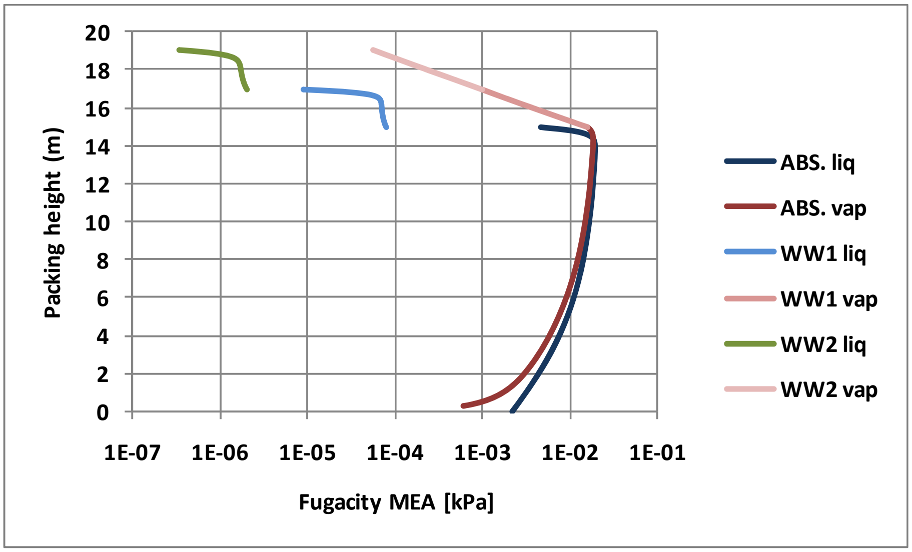
It can be seen that a large amount of water has condensed in the wash sections. The make-up water was set to 36 m^3/h at 15 °C, whereas at the bottom bleed the amount has increased to about 92 m^3/h at 30 °C. The sections contain water within the system and can thus be used for controlling the water balance.

Table 3.2 shows detailed simulation results for case AA1.

Table 3.2 Detailed simulation results for case AA1

STREAM	Temp.	Press	Flow rate	Vap. frac.	Mol frac. [CO_2]	Molfrac [H_2O]	Molfrac [MEA]	Molfrac [Inert]	Loading CO_2	Flow [CO_2]	Flow [H_2O]	Flow [MEA]	Flow [Inert]
Units	[°C]	[kPa]	[kmol/h]	[]	[]	[]	[]	[]	[mol/mol]	[kmol/h]	[kmol/h]	[kmol/h]	[kmol/h]
V2	45	101	56 179	NaN	3.30E-2	9.54E-2	0.00E+0	8.72E-1	~	1 854	5 362	0	48 964
V3	54	109	56 179	NaN	3.30E-2	9.54E-2	0.00E+0	8.72E-1	~	1 854	5 362	0	48 964
V4	57	103	56 564	1.00	3.28E-3	*1.31E-1*	*1.55E-4*	8.66E-1	~	185	7 406	9	48 964
P01	40	103	50 725	NaN	1.66E-2	8.73E-1	1.10E-1	0.00E+0	0.15	840	44 287	5 598	0
P02	50	109	50 340	0.00	4.98E-2	8.39E-1	1.11E-1	0.00E+0	0.45	2 508	42 242	5 589	0
V05	53	102	54 791	1.00	3.33E-3	*1.03E-1*	*9.45E-6*	8.94E-1	~	182	5 645	1	48 964
WW1	30	102	48 319	0.00	6.56E-4	9.98E-1	1.63E-3	0.00E+0	0.40	32	48 209	79	0
WW2	52	103	50 092	0.00	6.95E-4	9.98E-1	1.74E-3	0.00E+0	0.40	35	49 970	87	0
WW3	30	102	50 092	0.00	6.95E-4	9.98E-1	1.74E-3	0.00E+0	0.40	35	49 970	87	0
WW_Bleed	30	102	5 092	0.00	6.95E-4	9.98E-1	1.74E-3	0.00E+0	0.40	4	5 080	9	0
WW5	30	102	45 000	0.00	6.95E-4	9.98E-1	1.74E-3	0.00E+0	0.40	31	44 890	78	0
V06	49	101	53 472	1.00	3.40E-3	8.09E-2	5.55E-7	9.16E-1	~	182	4 326	0	48 964
P10	29	101	47 000	0.00	1.17E-4	1.00E+0	1.50E-4	0.00E+0	0.78	6	46 987	7	0
P11	47	102	48 319	0.00	1.23E-4	1.00E+0	1.57E-4	0.00E+0	0.78	6	48 306	8	0
P12	30	102	48 319	0.00	1.23E-4	1.00E+0	1.57E-4	0.00E+0	0.78	6	48 306	8	0
P13	30	102	3 319	0.00	1.23E-4	1.00E+0	1.57E-4	0.00E+0	0.78	0	3 318	1	0
P14	30	102	0	1.00	0.00E+0	0.00E+0	0.00E+0	0.00E+0	~	0	0	0	0
P15	30	102	45 000	0.00	1.23E-4	1.00E+0	1.57E-4	0.00E+0	0.78	6	44 987	7	0
MakeUp	15	101	2 000	0.00	0.00E+0	1.00E+0	0.00E+0	0.00E+0	NaN	0	2 000	0	0
P18	30	102	0	1.00	0.00E+0	0.00E+0	0.00E+0	0.00E+0	~	0	0	0	0

In figure 3.7 the fugacities of MEA is shown throughout the absorber and wash sections. The blue and green lines show the liquid phase fugacities (the equilibrium partial pressure of MEA) whereas the red lines show the actual partial pressure of the MEA vapour.



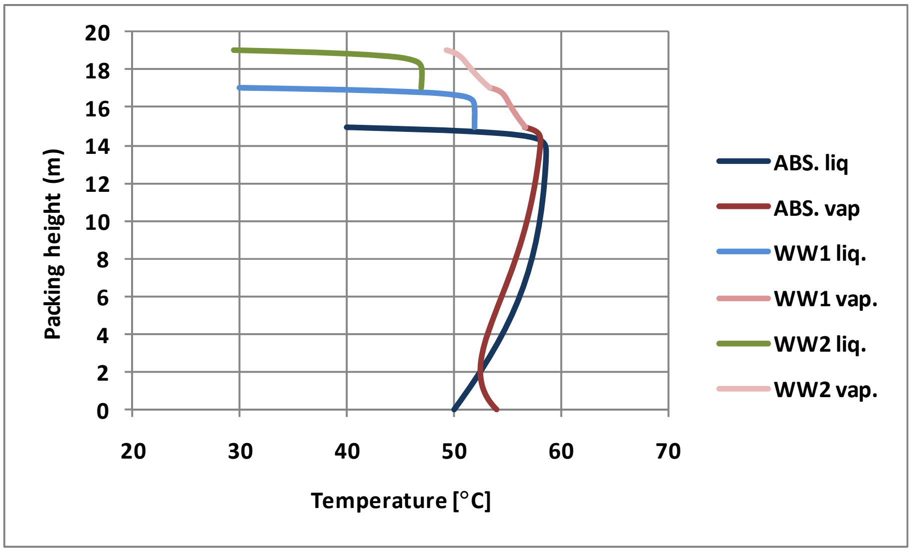
Abbreviations

ABS.:
CO_2 absorber column

WW1:
Water wash section 1

WW2:
Water wash section 2

Figure 3.7 Fugacity of MEA at the 3 sections, showing the thermodynamic driving forces available



Abbreviations

ABS.:
CO_2 absorber column

WW1:
Water wash section 1

WW2:
Water wash section 2

Figure 3.8 Temperature of MEA at the 3 sections, showing the thermodynamic driving forces available

From these simulations it is interesting to see that there are still significant driving forces for mass transfer to the liquid phase. We are thus far away from phase equilibrium. This is due to the gas film resistance correlation used in the simulator, taken from Bravo et al.

We do not know what the accuracy of this correlation is. Based on prior pilot testing the correlation seems to give good results out of the absorber top, prior to the water wash. We are assuming that the correlation gives quite high gas film resistance. The numbers are therefore conservative from our judgment. If we reduced the gas film resistance to maintain phase equilibrium at the top of the second water section, the resulting outlet concentration value would be less than 0.1 ppmv of MEA.

In figure 3.8 is shown the corresponding liquid and vapour temperatures along the columns. Also here it is shown that the determining heat transfer coefficient correlation shows a high resulting vapour temperature at the column outlets. Due to the rate based transfers, the vapour temperatures do not have time to approach the liquid temperature. The outlet vapour temperature is as much as 48 °C whereas the inlet wash temperature is at 30 °C, an 18 degree difference. The mass transfer coefficient uses a Reynolds analogy, and it is not known what the accuracy of this is either for the water wash sections. However, it can be noted that pilot plant results shows large difference in vapor and liquid temperatures at the absorber outlet prior to the wash sections.

3.1.6 Simplified water wash simulations

MEA system

We now want to compare the simulation results from CO2SIM with a simplified model developed in Matlab. The reason for model has earlier been compared with experiments in our lab pilot plant for different solvents.

Suppose we can assume that the gas leaving the water wash section is in equilibrium with the liquid wash water. Then we have from equation 3.1 for MEA

$$P_{MEA} = \gamma_{\mathrm{MEA}} P^{\mathrm{o}}_{\mathrm{MEA}}\, x_{\mathrm{MEA\_free}} \tag{3.3}$$

For γ_{MEA} a temperature function from the literature at infinite dilution is used.[13] The free MEA is a function of loading. If MEA is the only base in the water system the reaction with CO2 will ionize two molecules of MEA:

$$CO_2 + 2MEA = MEAH^+ + MEACOO^- \tag{3.4}$$

Defining the loading α_{MEA} as mol CO_2 reacted with MEA to total amount of MEA, the free MEA may be expressed as

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[13] Hoff, K.A., Juliussen, O., Falk-Pedersen O., Svendsen, H., “Modeling and Experimental Study of Carbon Dioxide Absorption in Aqueous Alkanolamine Solutions Using a Membrane Contactor.” Ind. Eng. Chem. Res., 2004.

$$x_{MEA\_free} = (1 - 2\alpha_{MEA})x_{MEA} \tag{3.5}$$

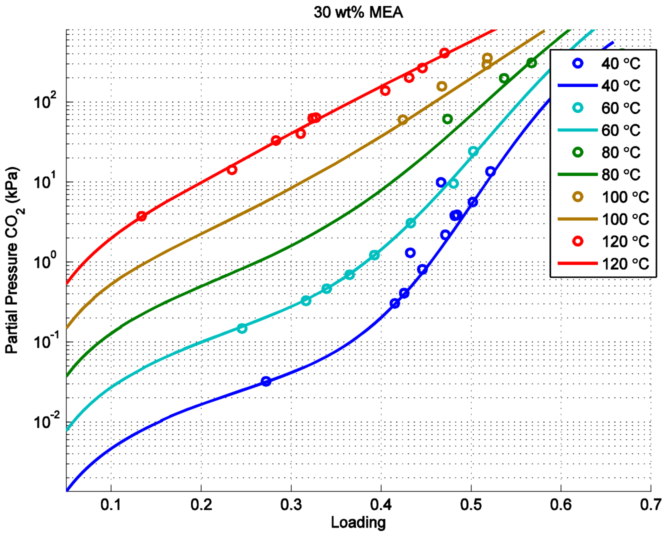

Figure 3.9 Experimental values (circles) compared with the model for various temperatures

The loading α_{MEA} is found by using a soft equilibrium model

$$P_{CO_2} = f(T, \alpha_{MEA}) \tag{3.6}$$

These models are developed and fitted to our own experimental values in the lab. The model for 30 wt % MEA is shown in figure 3.9.

For 90 % CO_2 capture the partial pressure of CO_2 in flue gases from natural gas and coal will be 0.4 and 1.2 kPa for respectively. Knowing P_{CO2} and temperature T, α_{MEA} is found by iteration of the function.

The gas will probably not be in equilibrium with the liquid phase at the outlet of the water wash section. The partial pressure of MEA will be greater than the equilibrium pressure with a factor f. For a given structured packing section this factor is correlated with the hydrodynamics, i.e. the gas and liquid flows. In the simplified simulations we have assumed that this factor is constant. From experiments in our lab pilot with a section of 2.1 m a factor of 2.5 has been used, which gave a good fit for the conditions there. Typically residence times are one second for the gas. A longer section will give higher residence times and a lower f-factor, but the effect of increasing the packing height has not been measured.

The model for the partial pressure of MEA out of a water wash section is then

$$P_{MEA} = f\gamma_{MEA}P_{MEA}^{sat}(1 - 2\alpha_{MEA})x_{MEA} \tag{3.7}$$

If there are several sections with water wash the model assumes that equation 3.7 is valid for each stage. The Matlab model now simulate a dynamic situation where we start with pure water in the water wash sections and a constant liquid flow of pure water in the top, and a constant gas flow coming from the absorber and let the system go to steady state such that the amount of amine coming into the water wash system is equal to the amount of amine going out of with the bleed flow in the bottom. The model assumes constant temperature in all sections and that the flow of fresh water is both added water and water condensate.

Now, in order to compare with the result with CO2SIM, we have used the following parameters:

Temperature: 53.5 °C, which is the average temperature of the gas phase.

Fresh water flow: 4198.5 kmol/h, which is the average of the bleed from the two sections.
This fresh water flow corresponds to β = 8.57 mol % of the inert flue gas.

In the first two columns in table 3.3 a comparison with CO2SIM case AA1 with an f-factor of 2.5 is shown. The deviation is quite large. In order to obtain results similar to CO2SIM an f - factor of 14 must be used. (The small deviation in the feed ppm is due to the temperature difference in the gas phase inside the water wash and the flow from the absorber). Even if a factor of 2.5 is more in line with experimental data, we will first use the more conservative factor of 14.

Table 3.3 Comparison of concentrations (ppmv) using simplified model and CO2SIM

	CO2SIM	f=2.5	f=14	Flows in fig. 3.5 and table 3.2
In WW sec1	155,5	153,6	153,6	V4
In WW sec2	9,45	1,74	9,72	V05
Out WWsec2	0,56	0,02	0,58	V06

f = (Partial pressure of MEA/Equilibrium pressure of MEA with the liquid phase)
β = 100·[Fresh water flow (kmol/h)/Dry inert gas flow (kmol/h)]

Table 3.4 MEA conc. (ppmv) simulation for the different cases f = 14.0, β = 8.57mol %

	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
In WW sec1	153,542	132,229	107,746	154,020	132,707	111,307	62,122	53,055	42,045	63,378	54,291	45,205
sec1/sec2	9,781	8,346	6,712	9,676	8,331	6,941	0,929	0,800	0,607	0,936	0,822	0,692
sec2/sec3	0,621	0,525	0,417	0,606	0,521	0,431	0,014	0,012	0,009	0,014	0,012	0,011
Out WWsec3	0,037	0,031	0,024	0,036	0,031	0,025	0,000	0,000	0,000	0,000	0,000	0,000

See table 2.3 for the different process conditions used in simulations
Corresponding flows found in figure 3.5 and table 3.2
V4 = In WW sec1, V05 = sec1/sec2, V06 = sec2/sec3

Table 3.5 MEA conc. (ppmv) simulation results using f=14.0, β=4.0 mol %

	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
In WW sec1	153,544	132,230	107,747	154,022	132,708	111,308	62,122	53,055	42,045	63,378	54,291	45,205
sec1/sec2	20,907	17,841	14,349	20,683	17,809	14,839	1,991	1,714	1,299	2,006	1,761	1,482
sec2/sec3	2,809	2,375	1,886	2,741	2,359	1,953	0,064	0,055	0,040	0,063	0,057	0,049
Out WWsec3	0,337	0,283	0,222	0,325	0,280	0,230	0,002	0,002	0,001	0,002	0,002	0,002

In table 3.4 the results of using three stages are shown for all cases using the Matlab model. In the simulations the temperature is assumed to be 3.2 °C lower than the inlet gas stream temperature.

Because a fresh water fraction of $\beta = 8.57$ is quite large, we also simulated with $\beta = 4.0$. The results from this simulation are shown in table 3.5.

Table 3.6 MEA conc. (ppmv) simulation results using f=2.5 β=4.0 mol %

	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
In WW sec1	153,542	132,229	107,746	154,020	132,707	111,307	62,122	53,055	42,045	63,378	54,291	45,205
sec1/sec2	3,741	3,193	2,568	3,701	3,187	2,655	0,356	0,306	0,232	0,358	0,314	0,265
sec2/sec3	0,091	0,077	0,061	0,089	0,077	0,063	0,002	0,002	0,001	0,002	0,002	0,002
Out WWsec3	0,002	0,002	0,001	0,002	0,002	0,001	0,000	0,000	0,000	0,000	0,000	0,000

Corresponding flows found in figure 3.5 and table 3.2: V4 = In WW sec1, V05 = sec1/sec2, V06 = sec2/sec3

For comparison we also run the simulations with a factor of 2.5. Table 3.6 shows the results from this simulation.

The results show that for MEA it is possible to go very low in terms of emissions, even to the low level of 0.01-0.2 ppm. The tables also show that the number of stages is most important then the gas temperature and finally the amount of water (β).

The simulations do not include any liquid entrainment, so for MEA the main focus should be to avoid mist and droplet entrainment. The aerosol formation in the absorber and its penetration through water wash sections including demisters can not be calculated. High opacity plumes from an MEA based CO_2 absorber with three washing trays have been described by Arnold et al (1982).[14] Aerosol concentrations in such plumes are normally larger than 20 mg/m^3. It is therefore not be unreasonable conservative to assume that the aerosol emission from a new plant can be in the order of 1 – 2 mg/m^3 after to water wash sections including demisters. Based on 30 % MEA in the droplets the corresponding emission of MEA would be 0.3 – 0.6 mg/m^3 or 0.1 – 0.2 ppm. Here the MEA content in the droplets is probably lower, but the droplet emission might be higher.

AMP/PZ system

For the system AMP and Piperazine equation 3.1 is again the starting point. Because AMP do not form carbamate ($AmCOO^-$) only one AMP molecule goes into the reaction with CO_2 and we have:

$$x_{AMP\_free} = (1-\alpha_{AMP})x_{AMP} \tag{3.8}$$

Piperazine is a diamine which forms carbamate, and the effect of loading is difficult to predict without having a full speciation of all the components. To simplify, we can assume that the amount of free piperazine amine groups is $(1-2\frac{\alpha_{Pz}}{2})$. The probability of having two free amino groups on the same molecule is then $(1-\alpha_{Pz})^2$ and we get:

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[14] Arnold, D.S., Barrett, D.A., Isom, R.H.: "CO, Can. Be Produced From Flue Gas." Oil and Gas Journal, Nov 22, 1982, p. 130.

$$x_{Pz\_free} = (1-\alpha_{Pz})^2 x_{Pz} \tag{3.9}$$

In order to account for a deviation from equilibrium a factor, *f*, is again included into the model. The model then becomes:

$$\begin{aligned} P_{AMP} &= f\gamma_{AMP} P_{AMP}^{sat}\left(1-\alpha_{AMP}\right) x_{AMP} \\ P_{Pz} &= f\gamma_{Pz} P_{Pz}^{sat}\left(1-\alpha_{Pz}\right)^2 x_{Pz} \end{aligned} \tag{3.10}$$

In order to get the loading for AMP we have used a soft equilibrium model (equation 3.6). For pure piperazine we do not have a model, but we have a model for a mixture of 3 mol AMP/l and 1.5 mol PZ/l in water. Using a combination of these two models one may calculate an approximate loading also for Piperazine.

Table 3.7 AMP+PZ conc. (ppmv) simulation results using f = 14 and β = 8.57 mol %

AMP	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
In WW sec1	416,660	399,239	383,051	413,345	396,506	381,222	177,060	169,535	162,571	174,619	167,422	160,585
sec1/sec2	445,569	427,276	410,551	441,347	423,753	408,133	81,512	78,748	76,355	79,665	77,154	74,853
sec2/sec3	318,315	305,497	293,991	314,788	302,527	291,912	26,527	25,839	25,311	25,711	25,132	24,640
Out WWsec3	170,884	164,144	158,218	168,702	162,292	156,902	6,962	6,830	6,750	6,699	6,601	6,531

Piperazine	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
In WW sec1	138,887	133,080	127,684	137,782	132,169	127,074	59,020	56,512	54,190	58,206	55,807	53,528
sec1/sec2	80,837	77,707	75,008	79,686	76,725	74,302	3,676	3,584	3,515	3,560	3,483	3,419
sec2/sec3	22,454	21,649	21,015	22,003	21,259	20,726	0,114	0,114	0,114	0,109	0,109	0,109
Out WWsec3	5,137	4,966	4,844	5,008	4,853	4,760	0,003	0,003	0,004	0,003	0,003	0,003

See table 2.5 for the different process conditions used in simulations
Corresponding flows found in figure 3.5 and table 3.2: V4 = In WW sec1, V05 = sec1/sec2, V06 = sec2/sec3

Table 3.8 AMP+PZ conc. (ppmv) simulation results using f = 2.5 and β = 8.57 mol %

AMP	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
In WW sec1	416,616	399,198	383,013	413,301	396,465	381,184	177,058	169,533	162,569	174,617	167,420	160,584
sec1/sec2	114,000	109,440	105,370	112,687	108,331	104,588	14,994	14,496	14,069	14,643	14,193	13,783
sec2/sec3	22,784	21,911	21,166	22,444	21,620	20,956	0,949	0,927	0,910	0,918	0,900	0,884
Out WWsec3	3,907	3,764	3,646	3,837	3,703	3,602	0,057	0,056	0,055	0,054	0,054	0,054

Piperazine	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
In WW sec1	138,872	133,066	127,671	137,767	132,155	127,061	59,019	56,511	54,190	58,206	55,807	53,528
sec1/sec2	14,692	14,126	13,640	14,479	13,944	13,509	0,656	0,640	0,628	0,636	0,622	0,610
sec2/sec3	0,776	0,749	0,728	0,760	0,735	0,717	0,004	0,004	0,004	0,003	0,003	0,003
Out WWsec3	0,039	0,038	0,037	0,038	0,037	0,036	0,000	0,000	0,000	0,000	0,000	0,000

Table 3.9 AMP+PZ conc. (ppmv) simulation results using f=2.5 and β = 4.0 mol %

AMP	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
In WW sec1	416,737	399,311	383,117	413,420	396,575	381,287	177,060	169,534	162,570	174,618	167,422	160,585
sec1/sec2	233,275	223,910	215,512	230,678	221,721	213,976	32,050	30,984	30,070	31,302	30,339	29,461
sec2/sec3	90,955	87,436	84,395	89,679	86,348	83,613	4,293	4,190	4,114	4,154	4,068	3,998
Out WWsec3	27,937	26,891	26,018	27,475	26,494	25,729	0,514	0,506	0,502	0,493	0,488	0,485

Piperazine	AA1	AA2	AA3	AB1	AB2	AB3	BA1	BA2	BA3	BB1	BB2	BB3
In WW sec1	138,904	133,096	127,698	137,798	132,184	127,088	59,020	56,511	54,190	58,206	55,807	53,528
sec1/sec2	31,395	30,187	29,149	30,939	29,797	28,869	1,406	1,370	1,344	1,361	1,332	1,307
sec2/sec3	3,520	3,396	3,300	3,447	3,332	3,252	0,017	0,017	0,017	0,016	0,016	0,016
Out WWsec3	0,359	0,347	0,339	0,349	0,339	0,333	0,000	0,000	0,000	0,000	0,000	0,000

In table 3.7 the results are shown with the same conditions as in the CO2SIM simulation for MEA in table 3.4 with a fresh water mol fraction = 8.57 % and a factor f = 14. By comparing the tables it is clearly seen that the emission of AMP becomes much higher than the emission of MEA after two washing stages. Calculation of water wash separation efficiencies from the two tables will show that for two stages efficiencies for MEA varies between 99,976- and 99,9997 %, while efficiencies for AMP varies between 59 and 96 % and for PZ between 96,3 and 99,994 %.

In table 3.8 we changed to f = 2.5 which is more in line with measurements performed in lab scale. We see that low temperatures combined with 2 stages and high amount of water gives a value below 1 ppmv for AMP. The effect of using one more stage is substantial and should be recommended for this amine.

Table 3.9 shows that less fresh water flow (lower β) gives higher emissions of AMP.

We see from the tables that AMP is much more difficult to capture in a water wash compared to Piperazine even if the vapour pressure for the pure components is lower (figure 3.3). The reasons are large difference in activity coefficient and loading. The same is even more the case when comparing AMP to MEA.

Higher packing sections would have lowered the temperature of the gas phase. In terms of effective wash sections the simulations show that it is more efficient with two sections with possibly lower $\eta_{eq.\ rel.}$ than one high section which gives higher $\eta_{eq.\ rel}$. As pointed out in chapter 5 there is a need for more work on this topic. Mass transfer correlations in the literature need to be verified against experimental data.

$\eta_{eq.\ rel}$ = Separation efficiency relative to the maximum efficiency at equilibrium condition

$$\eta_{eq.\ rel} = 100 \cdot (p_{in} - p_{out})/(p_{in} - p_{eq})$$

3.1.7 Comparison between solvent A (MEA based) and B (AMP based)

MEA vapour from solvent A is more easily absorbed with CO_2 in water compared to the AMP vapour from solvent B.

Dissolved in water AMP is more volatile than MEA, because of the large solubility of MEA in water compared to AMP.

These two favourable characteristics of solvent A implies a better performance in terms of capture efficiency by the water wash section and also probably slightly lower energy consumption compared to solvent B

3.2 Chemical wash system assessment (WP 2b)

Absorption of ammonia and amines in an acid wash

Components that are captured in the acid wash will to a large extent be volatile amines and ammonia. A pH of 3-4 is recommended for acid wash of ammonia. This pH range is probably equally applicable to amine components.

Equilibrium pressure of a basic component (amines, NH_3) in an aqueous solution depends on pH, concentration and temperature. If sulfuric acid is used to control pH, the reaction with ammonia is given by equation 3.11 (corresponding reactions with amines):

$$2NH_3 + 2H^+ + SO_4^{2-} \Rightarrow 2NH_4^+ + SO_4^{2-} \qquad (3.11)$$

Ionization constant K_a for ammonia in water:

$$K_a = C_{NH3} \cdot \frac{C_{H+}}{C_{NH4+}} = 10^{-9.25} \qquad (3.12)$$

Equation is valid for ideal (diluted) solutions; the activity has to be used for concentrated solutions.

Reaction with an amine R_1R_2NH:

$$2R_1R_2NH + 2H^+ + SO_4^{2-} \Rightarrow 2R_1R_2NH_2^+ + SO_4^{2-}$$

The ionization constant K_a for alcanol amines in water is similar to equation 3.12:

$$K_a = C_{R1R2NH} \cdot \frac{C_{H+}}{C_{R1R2NH2+}} \qquad (3.13)$$

The ionization constant K_a for alcanol amines is mostly in the range 9-11 which means that the concentration of free amine will be very low.

The equilibrium pressure, P^{eq} , is given by the equation:

$$P^{eq} = H^{'} \cdot C \cdot \{\alpha/(1+\alpha)\} \cdot 2 \cdot C_s \qquad (3.14)$$

$H^{'} = H/C$
H = Henry's constant
C = concentration of solute (ammonia, amines)
$\alpha = K_a/10^{-pH}$
C_s = concentration of dissolved solute

For ammonia:

Henry's constant H (bar) = $H^{'} \cdot C_t = 0.268 \cdot \exp(0.0525 \cdot t)$, t = temperature ^{o}C
Ionization constant $K_a = 10^{-9.25}$

The figures 3.10, 3.11 and 3.12 show the partial pressure of ammonia as a function of pH with 0.1, 0.5 and 5 M $(NH_4)_2SO_4$ in the acid wash solution. The ammonia pressure increases with temperature and pH.

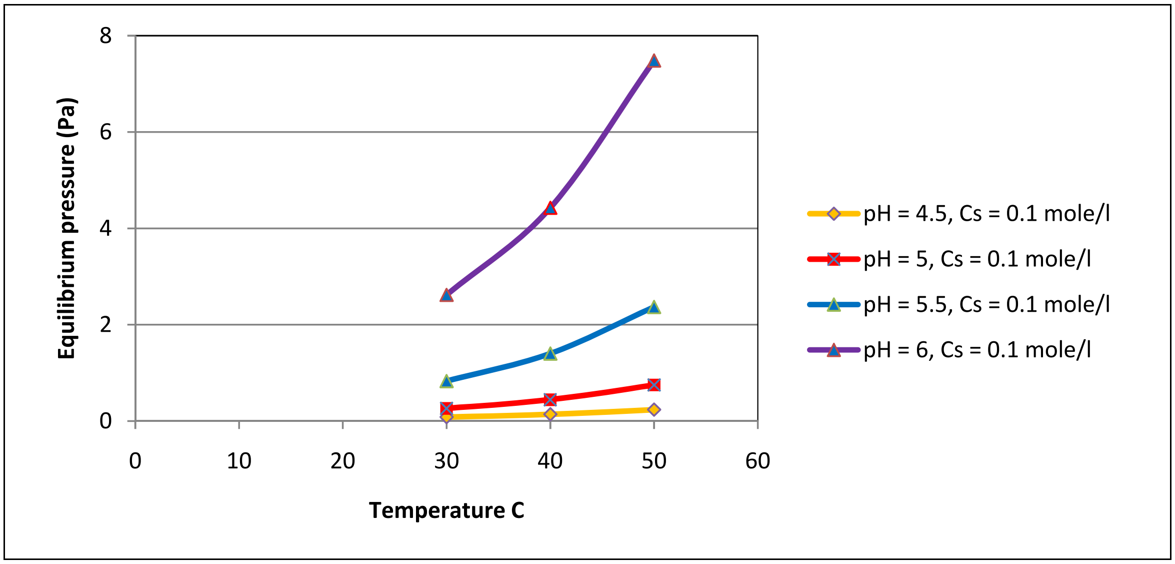


Figure 3.10 **Equilibrium pressure of ammonia at ammonium sulphate concentration 0.1 mole/l in the pH range 4.5-6**

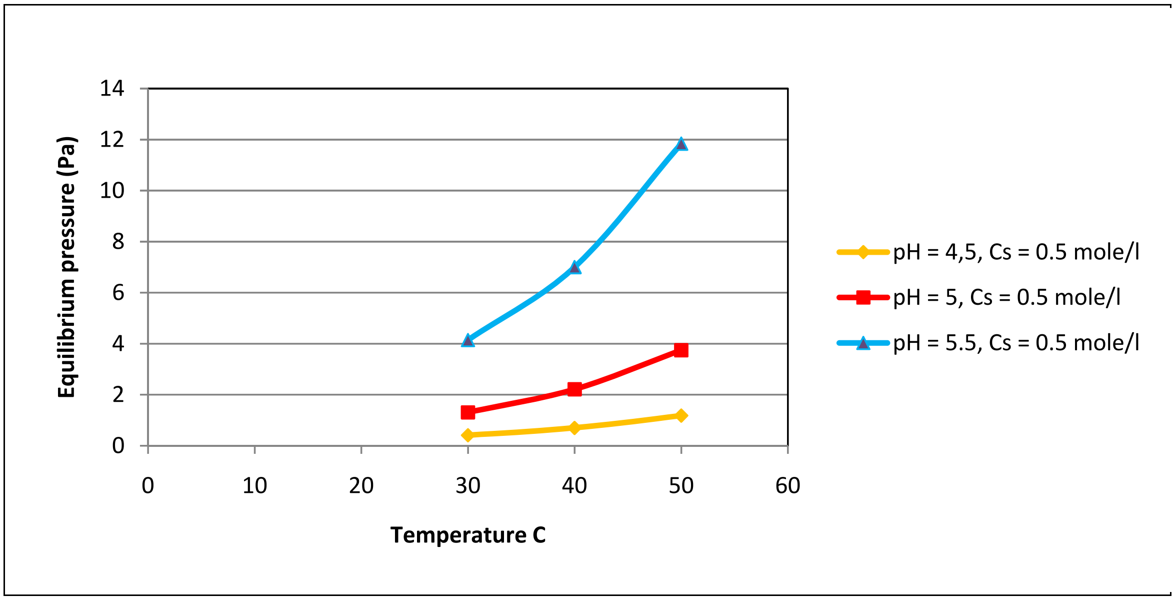


Figure 3.11 Equilibrium pressure of ammonia at ammonium sulphate concentration 0.5 mole/l in the pH range 4.5-5.5

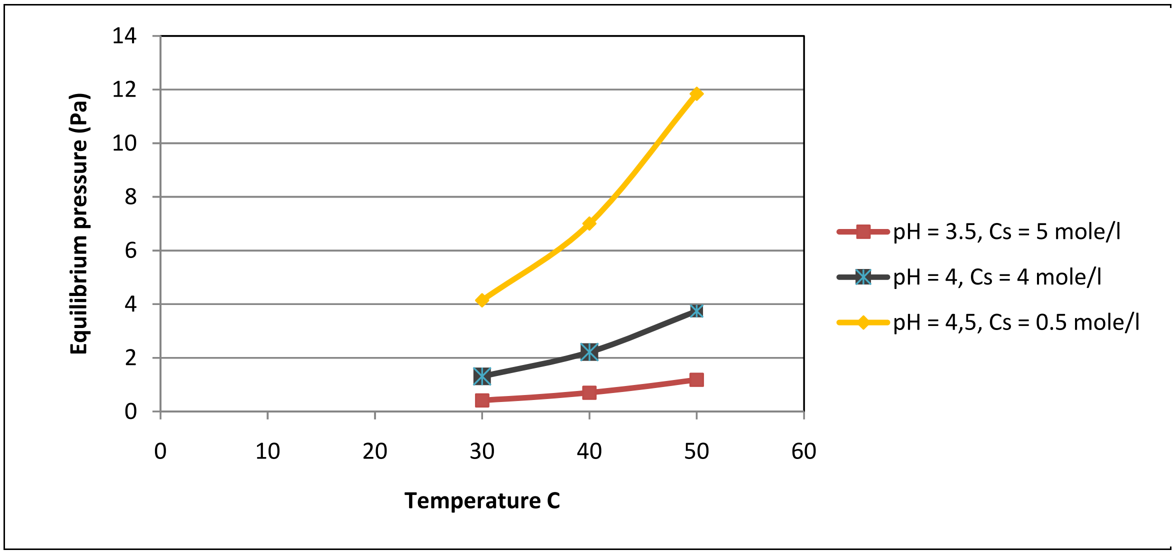


Figure 3.12 Equilibrium pressure of ammonia at ammonium sulphate concentration 5 mole/l in the pH range 3.5-4.5

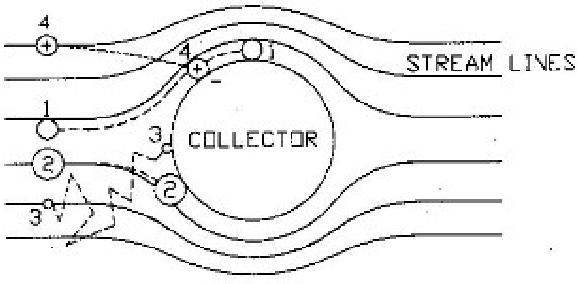
The equilibrium vapour pressure of amine is expected to be much lower than the corresponding vapour pressure for ammonia. While the physical properties of ammonia and amine components differ, it would seem likely that the efficiency of an acid wash would be similar for amines and ammonia.

The efficiency of acid washes for amine components and possible nitrosamines and nitramines is discussed in chapter 3.4.1 Acid wash and UV treatment.

3.3 Demister system assessment (WP 2c)

3.3.1 Theory

Mist or droplets are mainly collected in the three different ways 1-3 as shown in figure 3.13. In particular cases drops are also separated by electrostatic forces 4.



1. Inertial Impaction
2. Direct Interception
3. Brownian Movement/Diffusion
4. Electrostatic attraction

Figure 3.13 Droplet collection principles for a fibre[15]

Inertial Impaction
Large droplets (3 microns or larger) are collected when their momentum prevents them from following the gas streamlines around a fibre. The momentum of the droplet causes it to leave the streamline and strike the fibre and become collected. Since momentum is the product of mass and velocity, it follows that large droplets will be collected more efficiently than small droplets travelling at the same velocity.

Direct Interception
Direct interception of a droplet occurs when the size of the particle allows it to follow the gas streamline around an object in its path. As the particle follows the gas streamline around the object it may come sufficiently close to the object such that it will touch the object and become collected. Interception as a collection mechanism is less important than inertial impaction.

Brownian Diffusion
Extremely small acid particles or mist are so small that they do not follow the gas streamlines but exhibit a random path as they collide with gas molecules. These submicron particles will be collected when they collide or touch an object.

Examples of mist eliminators are vane type and knit-mesh type entrainment separators and candle filter elements packed with glass fibres. These are shown in the next chapters.

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[15] http://www.sulphuric-acid.com/techmanual/strong%20acid/sa_mist.htm

3.3.2 Knit-mesh type demisters

The separation principle for this type demister is inertial impaction because gas acceleration around wires combined with inertia of the drops make them collide (impact) on the thin wires, which are obstacles in the gas stream. See figure 3.13.

Knit-mesh type demisters shown in figure 3.14 are made up from knitted materials with interlocking asymmetrical loops of metal or plastic with typical wire diameters being 0.1 - 0.3 mm. Such demisters have high free volumes (typically 98 – 99 %) along with high removal efficiencies for drops larger than 10 µm and low pressure drop.

Optimal gas velocity will depend on operating temperature, pressure and pressure drop. Under normal operating pressure drop of is less than 250 Pa.

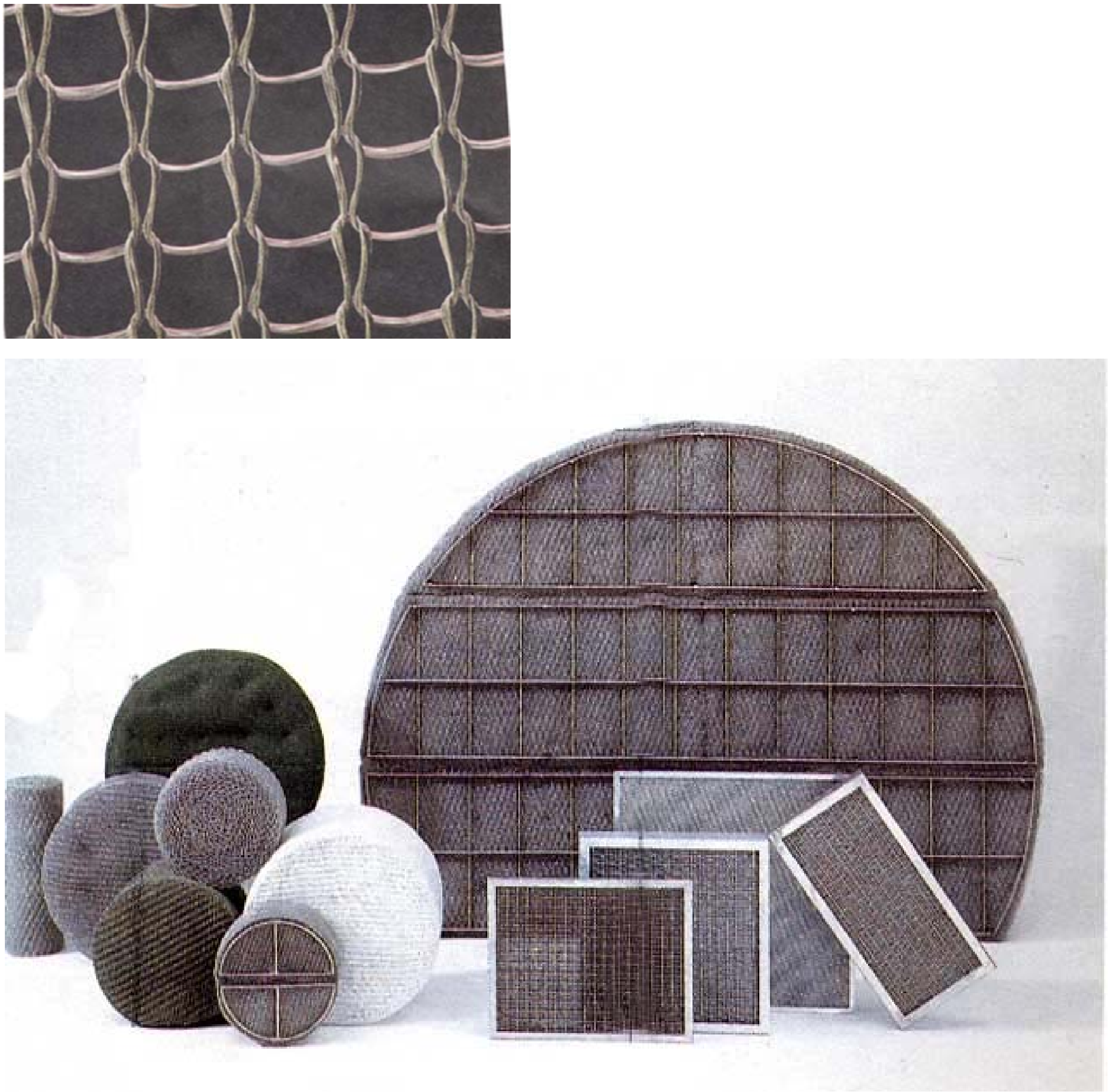

Figure 3.14 Knit-mesh type demisters

Mesh pads are efficient in removing particles of diameter 5 µm or larger. Mesh pads are dimensioned for relatively high gas velocities, which relies on the fact that the diameters of the particles that can follow the gas streamline decrease as gas velocity increases. However, at higher gas velocities, the possibility of droplet re-entrainment occurs. At lower gas velocities, the momentum of the particle decreases which decreases the collection efficiency. The effective operating of a typical mesh pad is approximately 30- to 110 % of design gas flow.

Mesh pads are usually made of woven metal wire that is crimped and formed into a flat pad and fitted into the tower. The mesh is held together by a grid place above and below the pad.

To enhance the collection efficiency of a mesh pad, glass or PTFE fibres can be co-knitted with the wire to form a composite pad. The smaller diameter glass or PTFE fibres increase the number or targets in the pad without the need to make the pad denser, which increases pressure drop.

Glass fibre materials can be fabricated hydrophilic or hydrophobic by choice. Amine aerosols are hydrophilic in it self and will therefore more easily stick to hydrophilic fibres. Even hydrophobic fibres will probably become hydrophilic if exposed to amines for a long time.

3.3.3 Vane type mist eliminators

Inertial impaction is also separation principle for vane type mist eliminators as shown in figure 3.15 where drops impact on baffle plates. Such separators are less efficient than the knit-mesh type but can operate at higher gas velocities. Pressure drop increase with velocity and is normally higher for the vane type.

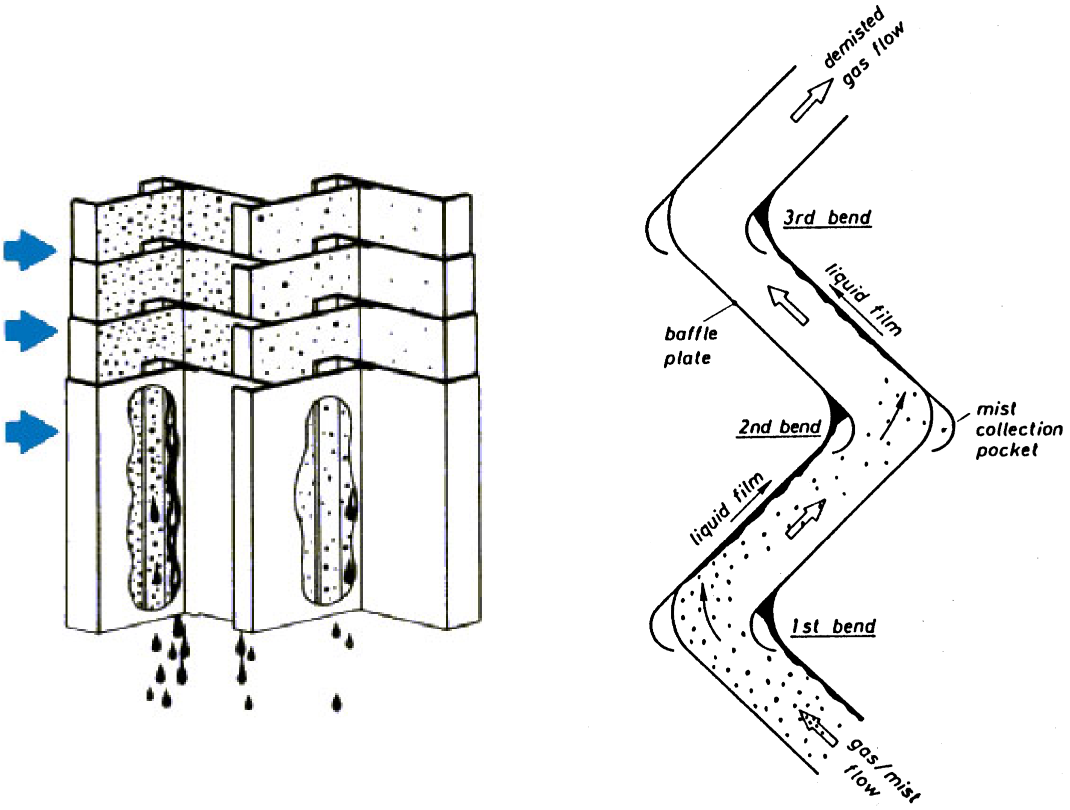

Figure 3.15 Vane type mist eliminator

3.3.4 Impaction candles

Impaction candles as shown in figure 3.16 utilize inertial impaction as the primary means of particle collection but they offer improved collection of particles in the 1- to 3 micron range that mesh pads are only capable of removing to a small degree.[15]

Impaction candles are made of glass fibres hand packed in between two metal cages or machine wound onto the inner cage with an outer cage added on top. Impaction candles are installed either in a hanging or standing position. Normal bed velocities are in the range of 1.27- to 1.63 m/s (250- to 320 ft/min). Since inertial impaction is the primary collection mechanism, the turndown capability is limited to 75 % of the design value.

Figure 3.16 Impaction candle

3.3.5 Brownian diffusion candle filter elements packed with glass fibres

It is at present not known to us if mist and aerosols may contribute to significant emissions from a CO_2 capture plant. In a plant with an efficient water-wash system and acid wash mist and aerosols may however become one of the main sources of emissions.

More densely packed fibrous beds are efficient in capturing sub-micron fumes and aerosols. There are several commercial providers for such technology. The main operating cost related to such technology is higher pressure loss in the system. The utilized materials are also expensive and may have a significant capital cost.

All three collection mechanisms are active in Brownian diffusion candles shown in figure 3.17, but Brownian diffusion is the mechanism which allows these elements to achieve the high collection efficiencies.[15]

Design bed velocities are very low and range from 0.025 to 0.2 m/s depending on the pressure drop and collection efficiency desired. In contrast to the other type of mist eliminators, the collection efficiency of Brownian diffusion candles increases as the gas velocity decreases. At lower velocities the residence time of the mist particles in the fibre bed increases so the chance that they will be captured increases.

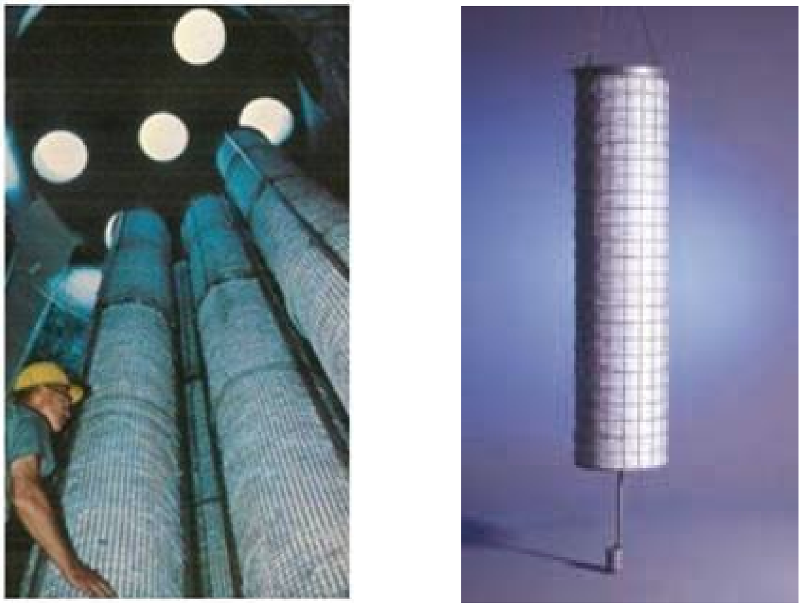

Figure 3.17 Brownian diffusion candles (Brink packed glass fibre filters)

Collection efficiency of aerosols that have penetrated through three demisters including two water wash stages might vary from 95- to 99.98 % depending on depth and density of packed fibres, diameter of singe fibres and gas velocity through the bed of fibres. Two suppliers of such candle filter elements are:

Begg Cousland in Glasgow Scotland, UK (http://www.beggcousland.com/)

MECS, Inc. (http://www.mecsglobal.co.za/content/TFGI/Brink/)
earlier Monsanto Enviro-Chem Systems, Inc.

3.4 Other technology evaluation including emission destruction (WP 2d, e)

3.4.1 Acid wash and UV treatment

We regard a water wash as the most efficient step to control emissions from a CO_2 capture plant. It should be the first step in the emission control process. Solvent absorbed in the water-wash can also be returned to the process. Any other emission control technologies should come after the water wash or be integrated into the water wash cycle. In figure 3.18 is shown an advanced capture cycle. Components captured in the acid wash will not be returned to the absorption process. Components that are captured in the acid wash will to a large extent be volatile amines and ammonia.

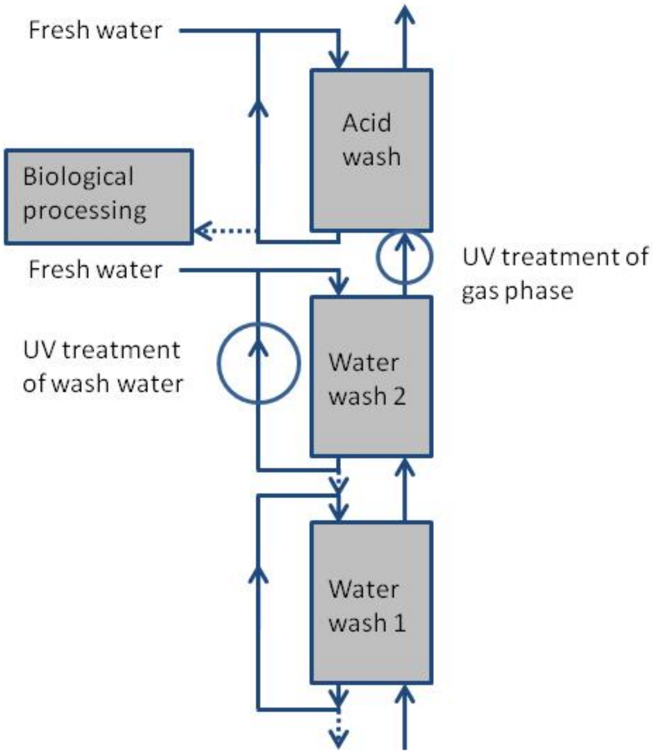

Figure 3.18 Advanced water wash configuration. (Demister is not included in the figure)

These components will probably not remain in the CO_2 absorption process even if they were returned back into the cycle. We therefore propose a biological treatment unit to handle the liquid from the acid wash. This would essentially be a waste stream.

In figure 3.18 we also consider two options for UV treatment of the streams. The most feasible option is UV treatment of the liquid stream in the water wash. Such a UV treatment should ensure that there is no build-up of nitrosamines and nitramines in water-wash liquid. As a result of this the water wash should maintain its efficiency in absorbing nitrosamines.

The more demanding option is treating the gas stream in the process. We have not calculated the energy and contact time required for such a step. This would however appear to be a technically more demanding option.

Photolysis by ultraviolet (UV) radiation is a common approach for removal of nitrosamines. As an example NDMA absorbs light strongly between 225 and 250 nm. This wavelength is at the lower end of the transparency of water to UV. The absorption results in a cleavage of the N—N bond, most likely via hydrolysis to dimethylamine and nitrous acid, or by forming nitroso and dimethylamine radicals. The major products of the reaction are the amine component and nitrite. In Appendix 5 is shown an example of a purification process incorporating UV-treatment.

In figure 3.18 we have suggested that UV treatment of the gas stream should come immediately before the acid wash. The UV treatment should reverse all nitrosamines and nitramines back to amine form. The acid wash can then absorb these components, thereby absorbing most components with amine functionality from the emissions.

We have not found any scientific literature describing the efficiency of acid washes for amine components. The literature we have found on ammonia absorption in acid washes suggests this step to be fairly efficient. One article describes removal rates of 96 % as usual.[16] Most amine has comparable basicity to ammonia. While the physical properties of ammonia and amine components differ, it would seem likely that the efficiency of an acid wash would be similar for amines and ammonia. This would again suggest that an acid wash can reduce the emissions of components with amine functionality by a factor of 10. If an acid wash reached equilibrium with the gas phase virtually all amine and ammonia would be absorbed.

A pH of 3-4 has been recommended for acid wash of ammonia.[13] This pH range is probably equally applicable to amine components. In a CO_2 capture process it may be that the ammonia emissions are significantly larger than those of amine components. There is therefore a risk that the acid wash will become saturated with ammonia. Acid must be added to maintain stable pH in the acid wash.

There is a possibility that nitrosamines and nitramines may form in the acid-wash section. This risk will most likely be a function of amine concentration, build up of nitrite and nitrate (and other species in equilibrium with nitrogen oxides) and pH. This risk can probably be controlled by limiting the build up of components in the acid wash. In other words controlling

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[16] R.W. Melse, A.V. van Wagenberg, J. Mosquera:" Size reduction of ammonia scrubbers for pig and poultry houses. Use of conditional bypass vent at high air loading rates". Biosystems Engineering (2006) 95 (1), 69–82

the circulation rate and the extent to which the waste stream is taken out. Since the acid wash is coming after a full water-wash system the build up of nitrate and nitrite may be very limited.

It would in principle be valuable to have some form of operation to remove nitrate and nitrite in the water-wash sections and acid-wash. This could for example be some form of scavenger, or component that leads to the precipitation of these species. We are however at present not aware of any technology or chemicals that would achieve this.

3.4.2 Electrostatic precipitators

Most industrial precipitators contains a row of thin vertical wires, and followed by a stack of large flat metal plates oriented vertically, with the plates typically spaced about 1 cm to 18 cm apart, depending on the application. The air or gas stream flows horizontally through the spaces between the wires, and then passes through the stack of plates.

A negative voltage of 30 - 50 kV is applied between wire and plate providing an electric discharge which ionizes the gas (corona) around the electrodes. Negative gas ions charge the particles in the gas sufficiently to be affected by the electric field. The charged particles migrate to the grounded collection plates following the negative electric field.

Figur 3.19 show example of an electrostatic separator. Such separators are in operation for removal of fly ash on coal fired power plants. A wet operating precipitator (WESP) would be needed for collection of aerosols from amine absorption columns. This would require a several huge units and extremely high capital costs for the CCM-project. Separation efficiency of a WESP on the actual sub micron aerosol droplets penetrating two water wash stages and three demisters might vary from 85- to 98 % depending on the specific surface area of the collecting electrodes, charging performance of the corona wires and operational electrical field voltage.

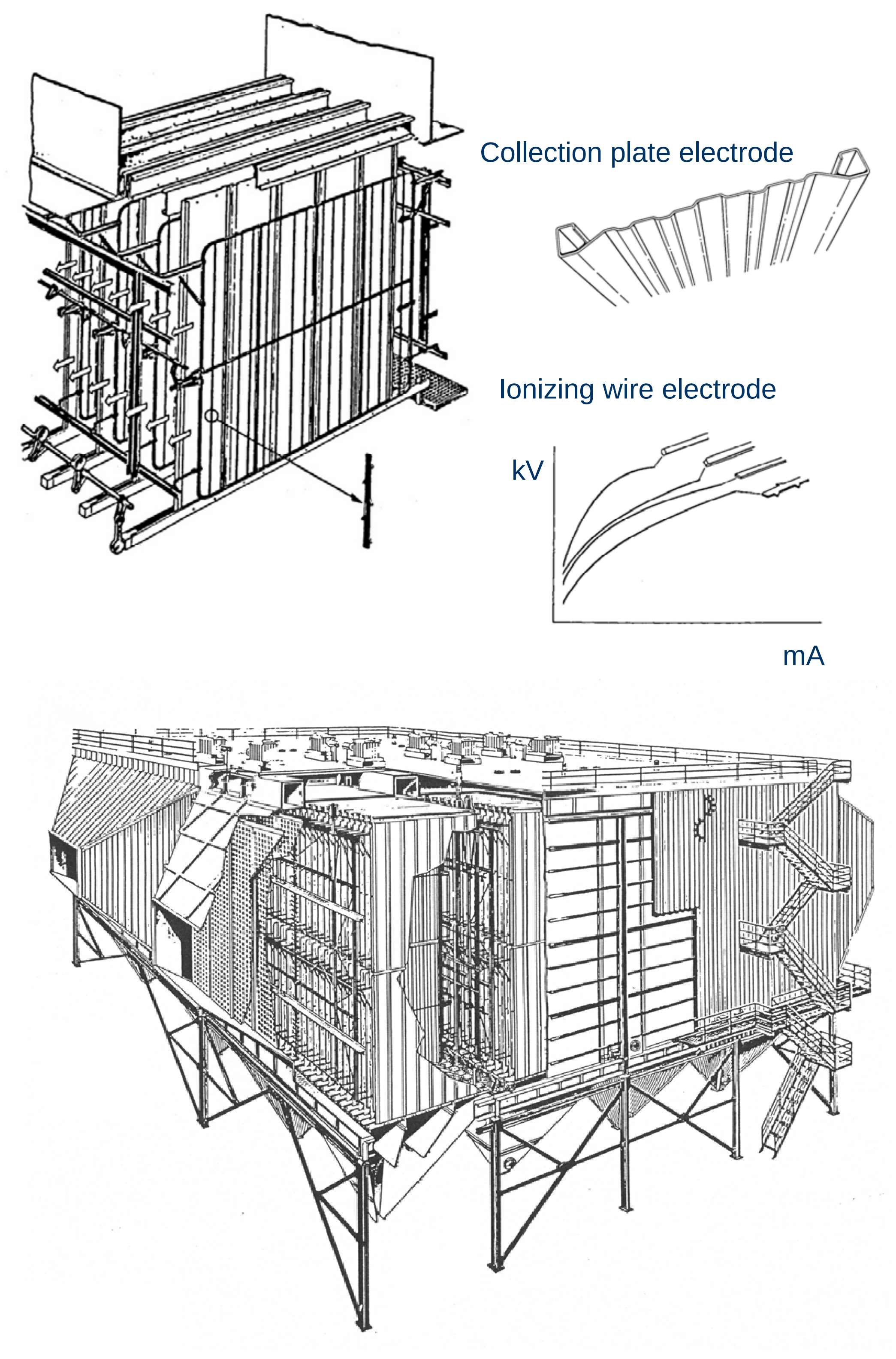

Figure 3.19 Example of dry electrostatic precipitator

3.4.3 Photochemical, electrochemical and ozone based technologies

There are a number of emission control/air purification technologies based on inducing chemical reactions with impurities in the gas phase. The Photochemical air purification (PAP) process developed at the University of Copenhagen, described in appendix 5 in this report, is just one example of such a technology. The PAP technology combines ozone generation, with UV-light and an electrostatic precipitator.

Such processes would in principle appear to have the potential to substantially reduce emissions from a CO_2 capture plant.

There would appear to be two main issues that must be addressed in order to decide if such concepts are suitable for a CO_2 capture plant. One is the residence time required for the given technology. Installation of a step with a high residence time would have significant implications for the design of a CO_2 capture plant.

The second issue is the energy consumption required for such a technology. Reported energy requirement in appendix 5 seems to be very low.

The advantage of such process is that they do not result in a pressure loss or require any overall heating or cooling of the gas phase. In spite of possible clogging of UV-lamp surfaces such a PAP system should be easy to maintain.

The optimal integration of such technologies into a CO_2 capture plant should be studied in detail if their implementation was being considered. It may be that such a concept could be integrated with the water-wash system.

We believe such technologies should be considered as a next step if demisters, water-wash and acid-wash are found not to give the needed emission control efficiency.

Only pertinent and thoroughly performed laboratory and pilot experiments might demonstrate reliable emission levels of nitrosamines and nitramines. If it is found that these emission levels are too high, we would recommend the use of UV-light in combination with water-wash and acid-wash. The simplest use of UV-light would be treating the liquid phases in the water-wash and/or acid-wash and thereby reverse the formation of nitrosamines and/or nitramines. If the acid wash and UV-treatment is integrated properly, almost all potential nitrosamines, nitramines and nitrosamine/nitramine precursors could be captured in the acid-wash (the UV reversing the nitrosamines and nitramines to amines that will bind in an acid wash). The more demanding option would be to use UV light to treat the flue gas coming through the water wash. The main issue may be the residence time needed for a UV process.

3.4.4 Biofilters

Biofilters are utilized in the removal of ammonia and amine components from gas streams. In a CO_2 capture plant care must however be taken in avoiding/controlling contamination of the capture process with biological material.

Our recommendation is therefore that biological treatment be mainly considered for handling waste streams from the plant.

Appendix 3 describes application of bio filters and bio trickling filters to remove volatile organic compounds from waste air/gas may be utilized to remove and degrade discharged amines. In bio trickling filters, the compounds are captured in water before biodegradation in a trickling filter, while in bio filters the gas is treated directly. Both concepts rely on a mixed flora of micro organisms that degrade the organic compounds. Depending on the solubility of the amines in water and their biodegradability, the water in the discharged gas may be condensed and subsequently treated in a trickling filter.

3.4.5 Oxidation, combustion and decomposition

There are in principle a number of ways to induce the decomposition of degradation products. Many of these processes would however require higher temperatures and/or catalytic surfaces. Such technologies do not seem very suitable for the large gas streams in a CO_2 capture plant.

3.4.6 Adsorption

There are a number of processes based on adsorption of impurities in a gas phase on a solid adsorbent. Such a process could work efficiently in a CO_2 capture plant, and there are a number of adsorbent materials that could be considered. One difficulty is that fixed bed adsorption requires a regeneration step.

Fixed bed adsorbers may also have a significant pressure loss.

3.4.7 Membranes

In principle membranes could separate degradation products from air stream. We are however not aware of any membrane technology being offered for such an application.

3.4.8 Condensation

Condensation would require cooling of the entire gas stream. We do therefore not regard this as a real option. Condensation at low temperatures may play a role in sampling the emissions from a CO_2 capture plant.

3.4.9 Cold plasma processes

Another alternative is cold plasma technology. This technology is based on ionization of the gas phase irradiating it with electrons. The products can then be separated with electrostatic filters.

Cold plasma also called non-thermal plasma can be induced by surface or pulsed corona discharge. Energy consumption and required residence time must be established in order evaluate the applicability of such processes. They would probably not apply.

3.5 Ranking of emission control technologies for amine based CO_2 capture plants

Table 3.10 shows a ranking of emission reducing technologies for amine based carbon capture plants. A combination of water-wash and demisters receives the highest score.

Table 3.10 Ranking of emission control technologies for amine based CO_2 capture plants

Emission reducing technology	Ranking[a]	Comment
Water-wash	10	Integral part of emission control at a CO_2 capture plant
Demisters	10	Integral part of emission control at a CO_2 capture plant
Acid-wash	8	Is a established method for removal of ammonia from gas streams. Should also be efficient for removal of amine components.
UV in water wash/acid wash	7	Ultra-Violet light treatment is an established method for removal of nitrosamines from liquid streams.
Mist eliminators	7	Fibre beds that eliminate mist.
UV on flue gas through water-wash	6	Should be efficient in removal of nitrosamines and nitramines. Energy consumption and required residence time must be established.
Electrofilters	6	Electric field applied across filters.
Photochemical air purification	5	This concept combines UV, ozone generation and electrostatic precipitation. Energy consumption and required residence time must be established.
Cold plasma process	5	Based on ionization of gas with electrons. Energy consumption and required residence time must be established.
Biofilter	4	Biofilters are discussed in appendix 3 to this report.
Adsorption	3	Activated carbon and other adsorbents can be effective in capturing degradation products. An issue is how to effectively regenerate the adsorbing material.
Membranes	2	In principle membranes could separate degradation products from air stream.
Thermal oxidation	2	Probably not suited for gases with low concentrations of degradation products.
Catalytic combustion	2	Probably not suited for gases with low concentrations of degradation products.
Selective catalytic oxidation	2	Probably not suited for gases with low concentrations of degradation products.
Condensation	1	Would require cooling of the entire gas stream. Not regarded as feasible due to large need for cooling.
Catalytic decomposition	1	This is likely to require high temperatures and is not regarded as feasible.

a. The ranking indicates to which extent we believe an emission reducing technology to be suited for an amine based CO_2 capture plant.

Ten (10) indicates that a technology should be used for a CO_2 capture plant, while one (1) indicates that a technology is most likely not suited for this application.

Water-wash technology and demisters are discussed in detail in other parts of this report. Combinations of acid-wash and UV treatment are discussed in chapter 3.4.1.

4. STATUS DOCUMENTATION OF IDENTIFIED ERT

4.1 Water wash systems

4.1.1 General information

The purpose of the water-wash section is to minimize solvent losses resulting from both evaporation and mechanical entrainment.

In general, amine plant losses comprise mechanical (entrainment and leakages), evaporation, degradation and solubility losses.[17] The gas leaving the absorber will contain amines due to gas phase equilibrium (vaporization) and droplet carryover (resulting from entrainment). Solubility losses are governed by equilibrium between amine in a liquid hydrocarbon phase and the aqueous phase. Such losses can be neglected in carbon capture facilities at power plants.

The amine vaporization losses in the absorber can be calculated for each solvent based on vapour-pressure data of the specific amine and the flue gas stream temperature and pressure. The water wash system is used to manipulate the conditions of the flue gas/solvent equilibrium to return amine to the liquid phase and also to cool the gas for amine condensation. In the water wash, the water contacting the flue gas has a low amine concentration and a low amine vapour pressure. Thus, a new equilibrium is established and the amine is forced into the water phase. Additionally, the vaporization losses can be reduced by cooling the gas below the condensation temperature for the amine. Thus, condensed amine will coalesce into the counter-current water flow.

Water wash systems can also reduce entrainment losses from the absorber section if droplets carry over come in contact with the liquid water. When the flue gas flows through the wash section, amine droplets above a certain size (smaller droplets will follow the gas path through the packing) collide with obstacles in the trays or packing and coalesce with the counter current water flowing downwards and are collected with the water at the bottom of the wash section. However, it is generally not desirable that droplets from entrainment losses are introduced into the water wash section, since these droplets have a high amine concentration and reduce the efficiency of the water wash. This can be avoided if a demister is placed before the water wash section.

Another reduction mechanism for the water wash is to mix acid compounds in the water. Examples are sulphuric acid or CO_2. This can be regarded as a chemical wash and a special case of water wash. If for instance CO_2 saturated water is used in the wash system, the CO_2 will bind amines and thus achieve enhanced loss reduction.

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[17] A. Kohl, R. Nielsen:"Gas Purification". Gulf professional publishing, 1997.

4.1.2 Types of water wash systems

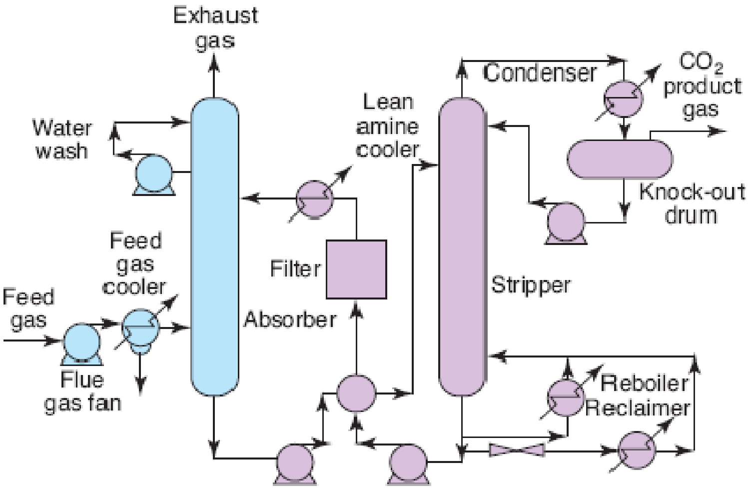

Figure 4.1 Principal sketch of water wash on top of absorber in CO_2 capture from flue gas by chemical solvent[18]

For CO_2 capture systems it is expected that the water wash is placed on top of the absorber, see figure 4.1

The water wash section is a recycle system where the water rich with amine is collected below the packing section and pumped via a cooler to the distributor above the packing. Amine is removed from the water-wash cycle by collecting water rich on amine before the cooler and returning it to the rich amine solvent stream leaving the absorber bottom. Make-up water is added in the circuit to keep water balance and to avoid too much build up of amine in the water wash section. This is required in order to keep a low amine vapour pressure in the water.

The most common scrubbing method is by using a counter-current flow of water; however other methods also exist such as co-current water-wash systems.[19]

Counter-current systems

Two typical flow schemes of counter-current water-wash systems are shown in figure 4.2. A set of trays or packing are placed above the lean amine feed point in the absorber as shown in the left figure, or as a separate vessel down stream of the absorber as shown to the right.

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[18] Intergovernmental Panel on Climate Change. 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L. (Eds.). Cambridge Univ. Press

[19] Stewart, E. J. and R. A. Lanning. 1994. Reduce amine plant solvent losses, Parts 1&2. Reprint from Hydrocarbon Processing, May 1994 issue, p 67-81 and June 1994 issue, p 51-54.

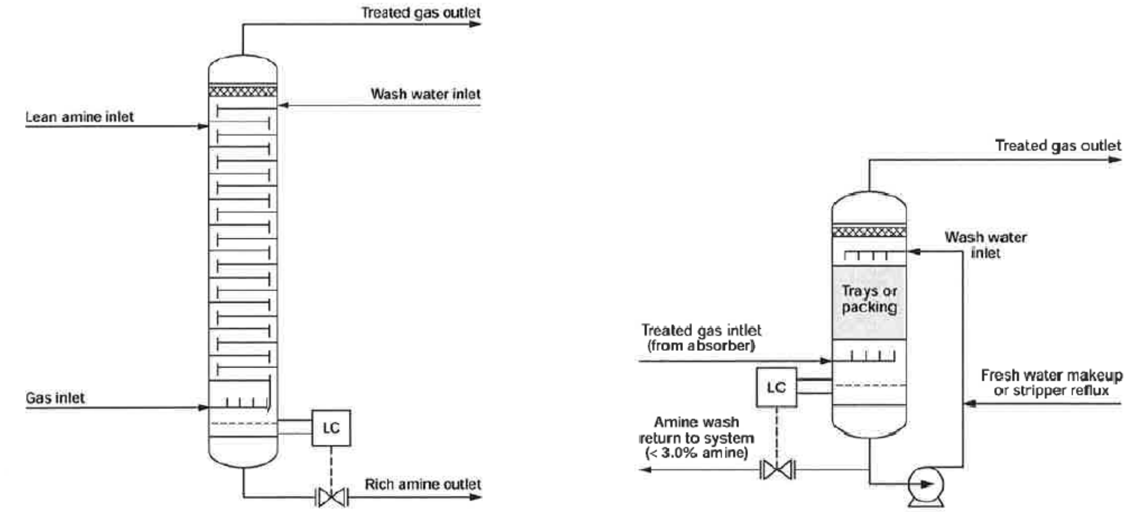

Figure 4.2 General schemes of counter-current water-wash-systems

Incorporated wash-tray design (left) and separate water-wash system (right).[17]

Co-current systems

Co-current water wash systems exist, but are more relevant for hydrocarbon liquid-treating systems.

4.1.3 Industry application

Water wash systems are commercially employed in various applications, the most common is within acid gas removal and gas and liquid hydrocarbon treating. The motivations for installing these systems have been purely economical. For CO_2 capture from combustion gases, industrial application of water wash systems is considered similar to the application of chemical absorption processes (amine plants) as described below.

Currently, CO_2 capture by absorption/stripping with aqueous monoethanolamine (MEA) is the benchmark technology for addressing CO_2 emissions from existing natural gas and coal-fired power plants. Chemical absorption by MEA is a derivative of extensively used technology for treating natural gas, hydrogen and liquid hydrocarbons. The technology is used commercially in combustion plants with gas rates equivalent to 20 MW. A summary of the most relevant industrial applications for CO_2 capture plants is found in appendix 1.

Maturity

The water-wash technology is in general considered a proven technology for removing CO_2 from combustion gases up to gas rates equivalent to about 1/10 of the size relevant for an absorber module at commercial scale for CO_2 capture and storage (CCS) application (100-400 MW). Here, proven technology is defined as a documented track record over the lifetime of the technology.[20] Thus, for commercial-scale CCS application, the technology is considered unproven and needs qualification. See chapter 4.4.1 for a maturity assessment according to API standards.

4.1.4 Scale up

Based on the discussion in the previous section, a scale-up factor of order 10 will have to be qualified since there is no operational experience with the use of scrubbers for treating combustion exhaust gases of this size.

In general, the critical aspects of scale-up relate to the impact of surface/volume and height/diameter ratios on flow patterns, gas/liquid dispersion and heat transfer. Typical problems may be of physical nature, chemical nature, or involve some aspects of both.

For chemical processes in general, some features considered to be of particular importance when moving from small-scale to commercial unit, are listed in table 4.1. In addition to the issues listed in table 4.1, presence of impurities not considered at laboratory scale could be encountered for a commercial operation and foul or poison solvents. Moreover, some impurities in recycle streams, e.g. solvent recycle, might accumulate over time and cause operational problems not foreseen at smaller scale.

Table 4.1 Scale-up issues[21]

Scale-up issues	*Challenges*
Shape and geometry of reactor	Fluid by-passing; Pressure drop; Stagnation zones resulting in changes in residence time distribution
Surface-to-volume ratios; Height-to-diameter ratios	Gradients of concentration and temperature; Flow patterns; Gas/liquid distribution
Materials of construction	Different contaminant levels

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[20] Det Norske Veritas AS:"Recommended Practice DNV-RP-J201 Qualification Procedures for CO_2 Capture Technology". Høvik, Norway, 2010

[21] Bisio, A. and R. Kabel:"Scale up of chemical processes. Conversion from laboratory scale tests to successful commercial size design". Wiley & Sons, 1985

Uniform gas and liquid distribution is indispensable for a large-size tower to obtain required performance. As the absorber cross sectional area increases, there is likely to be an increased number of challenges in maintaining uniform distribution of the solvent over the packing in packed columns, or of maintaining even distribution of solvent over large plate areas in plate columns. The most severe effects of uneven distribution in an absorber column on the capture performance can be summarized as:

- Uneven solvent flow distribution – If all the surface area of the packing is not wetted, then less surface area will be available for mass transfer from the flue gas to the solvent.

- Flue gas bypass – The flue gas will follow the path of least resistance. The parts of the tower with the greatest liquid flow will receive the least gas flow and the part with the least solvent will receive the most flue gas. This contributes to the loss of performance.

4.1.5 Energy requirement

The units that require energy are the pumps that circulate the water back to the top of the water wash section, pumps for the cooling water and for circulating make-up water.

There will also be an increased blower duty at the absorber inlet to overcome the pressure drop in the wash water packing. The gas pressure loss across washing sections is approximately 200 Pa per meter of packing.

Experience from pilot lab tests (water wash using almost isothermal conditions) combined with simulations at SINTEF indicates that the separation efficiency relative to the efficiency at equilibrium condition, $\eta_{eq.\ rel.}$, reaches 90 % after about 1.0 m of packing, and 99 % after 1.5 m of packing.* This may differ from one case to another, but was the reason why a 2 m packing have been used as a standard for one section of water wash at our labs. Standard HETP (Height Equivalent to a Theoretical Plate) for these types of packing is typically less than one meter (approximately 0.7m), which also indicates that 2 meter should be sufficient.

A rough estimate of packing height requirements for conventional absorption towers is given in chapter 4.1.7.

* $\eta_{eq.\ rel} = 100 \cdot (p_{in} - p_{out})/(p_{in} - p_{eq})$

4.1.6 Chemical requirement

There are no chemicals required for water wash. However, if chemical wash is regarded as part of the water wash, then acid compounds such as sulphuric acid or CO_2 are required. We have no references to chemical wash systems applied for amine based carbon capture.

4.1.7 Size

Typically commercial trayed and packed absorption column diameters generally do not exceed 11.5 m to 13 m to minimize potential flow mal-distribution problems.[22] To keep absorber diameters within this limitation to recover the CO_2 in the flue gas from a 400 MW natural gas combined cycle (NGCC) power plant, one might need to design two identical parallel trains. However, designing two trains have previously been considered uneconomical. A single-train conventional absorption tower could require a diameter of about 15 to 16 m. Such towers introduce flow distribution challenges as mentioned above.

The height of the water wash section is determined by the number of washing steps that depends on the emission limit requirements, the washing step performance, and the temperature. The number of steps and the performance will influence the tower height.
The height of a single-train conventional absorption tower could exceed 50 m where the water wash is typically about one third of this.

4.1.8 Waste

The water wash process produces waste water that has to be treated. Degradation products are not likely to be formed by water washing. This might become relevant if chemical wash is part of the process. A chemical wash included in the wash water section also introduce specific attention to treatment of these chemicals as possible waste products.

4.1.9 Process implications

Pressure drop
The gas pressure loss across washing sections is approximately 200 Pa per meter of packing elements. For a full-scale absorption tower, this corresponds to approximately 3 kPa pressure drop for the entire wash water section.

Process integration
The wash water section is an integrated part of the amine plants’ water cycle. The flue gas inlet temperature may influence evaporation in the plant. This may influence the water consumption.

Production stop
It is expected that scheduled shutdowns for the water wash coincide with the scheduled shutdowns for amine plant. The amine plant should be designed without affecting the availability of the power plant.

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[22] G. N. Choi, R. Chu, B. Degen, H. Wen, P.L. Richen and D. Chinn: “CO_2 removal from power plant flue gas – cost efficient design and integration study. In: Carbon Dioxide Capture for Storage in Deep Geologic Formations”. Vol. 1. D.C. Thomas and S.M. Benson (Eds). CO_2 Capture Project. Elsevier Ltd. 2005.

4.2 Demisters

4.2.1 General information

A demister utilises the different density between the substance to be removed (amine) and the fluid (exhaust gas out of the CO_2 absorber) it shall be removed from.

The exhaust gas from the amine absorber with the entrained amine droplets enters the demister. When flowing through the demister, the momentum of the droplets prevents them from following the gas around obstacles. As the gas is deflected, the droplets collide with obstacles in the demister and are removed while the gas continues through.

Both horizontal and vertical installations are possible. A horizontal/circular demister will have the same diameter as the absorber column or smaller if higher velocity is required. A vertical, cylindrical (candle type) will sit vertically inside the column. In that case, the gas is led up on the outside between the demister and the column wall, will travel horizontally through the demister and continue up through the centre of the column.

All the demisters looked at here are of the passive type. They have no moving parts, and require no input of energy in any form. Further, the demister types described are all commercial types. They are in use in all kinds of industries and applications and the demister principles must be said to be well proven. The specific type, shape and geometry of a demister will however vary based on the circumstances it operates in.

4.2.2 Types of demisters

Demisters come in different shapes, and the capture technology utilised in the differing types are somewhat different. However, the basic principle remains the same. The mist droplets collide with some kind of obstacle, small drops coalesce into larger droplets and in the end large drops is drained (drips off) from the surface.

Wire Mesh, Circular or Candle type
A wire mesh demister consists of tightly woven or “knitted” mesh pads, see figure 4.3.[23] The smaller the target, the smaller will the droplets that can be removed be. The reason for this is the fact that the droplets are “floating” in the gas stream and will to some extent be carried around the wire. Hence, velocity through a wire mesh is an important parameter.

Too small droplets relative to the wire or too low velocity will keep the droplet in the gas stream and carry it round the wire. Higher velocity or larger size will increase the possibility that it will collide with the wire. If the velocity is too high, liquid attached to the wire will be carried away again by the flowing exhaust and re-entrained in the gas stream. Figure 4.4 gives an overview of separation efficiency for various droplet sizes for a typical wire mesh demister. [24]

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[23] KnitMesh Technologies, www.knitmeshtechnologies.com/

[24] “The Engineered Mist Eliminator”, ACS Industries – Separations & Mass Products, http://www.acsseparations.com

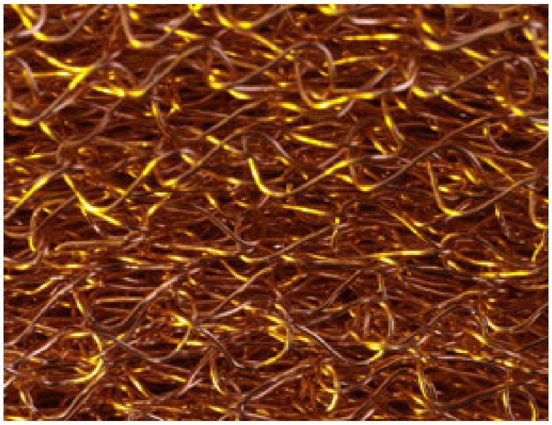
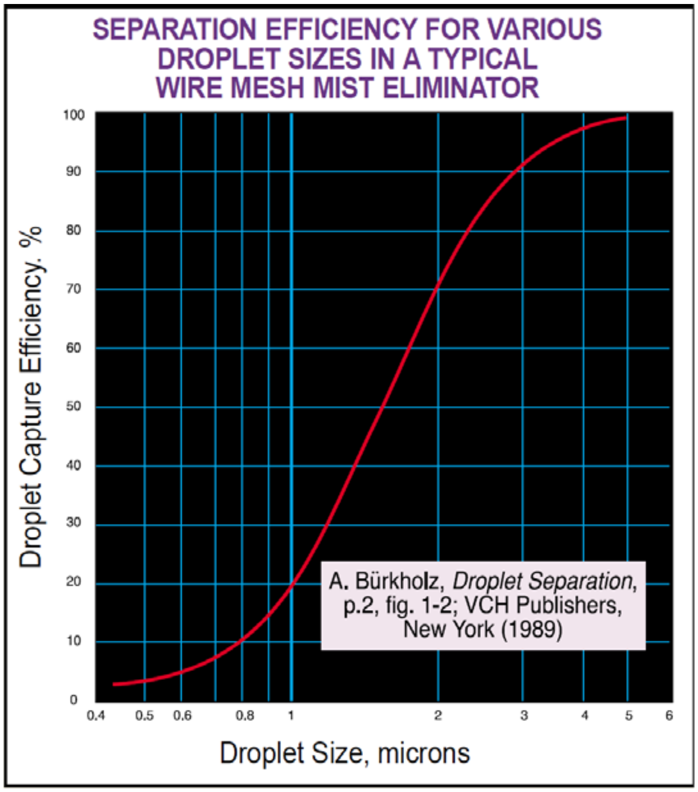


Figure 4.3 Typical Wire mesh



SEPARATION EFFICIENCY FOR VARIOUS DROPLET SIZES IN A TYPICAL WIRE MESH MIST ELIMINATOR

A. Bürkholz, *Droplet Separation*, p.2, fig. 1-2; VCH Publishers, New York (1989)

Figure 4.4 Separation efficiency for various droplet sizes

Wire mesh mist eliminator may remove 99.9% of droplets larger than 2 µm.

Velocity is a core element for a demister. A wire mesh demister can operate in a wide range of velocities typically 2 m/s up to 6 - 7 m/s. See figure 4.6. Exact velocity region is not possible to provide, as no information of droplet size distribution is known.

Vane type demisters

The vane type demister consists of corrugated steel plates placed so that the gas stream containing the mist is forced to bend from side to side to get through.[25, 26] For each bend, the droplets will hit the plate wall. Various additional features can be added to the vane demister to improve droplet collection, such as baffles and perforations in the vane plate. The perforations will make sure the droplets are transported into a "double wall", where the droplets are led into a void between the gas filled parts and drained separately from the gas stream. The risk of re-entrainment is thus reduced. Figure 4.5 is a simplified sketch of a detail of how a vane type demister may look like. Note that the bottom part only of the demister is shown. A vane demister consists of multiple corrugations.

Based on the expected small and sub micron particles and the removal capacity, a vane type demister seems not to be able to provide the removal efficiency required. As can be seen from figure 4.6, the velocity requirements are also stricter, with reduced flexibility as a result.

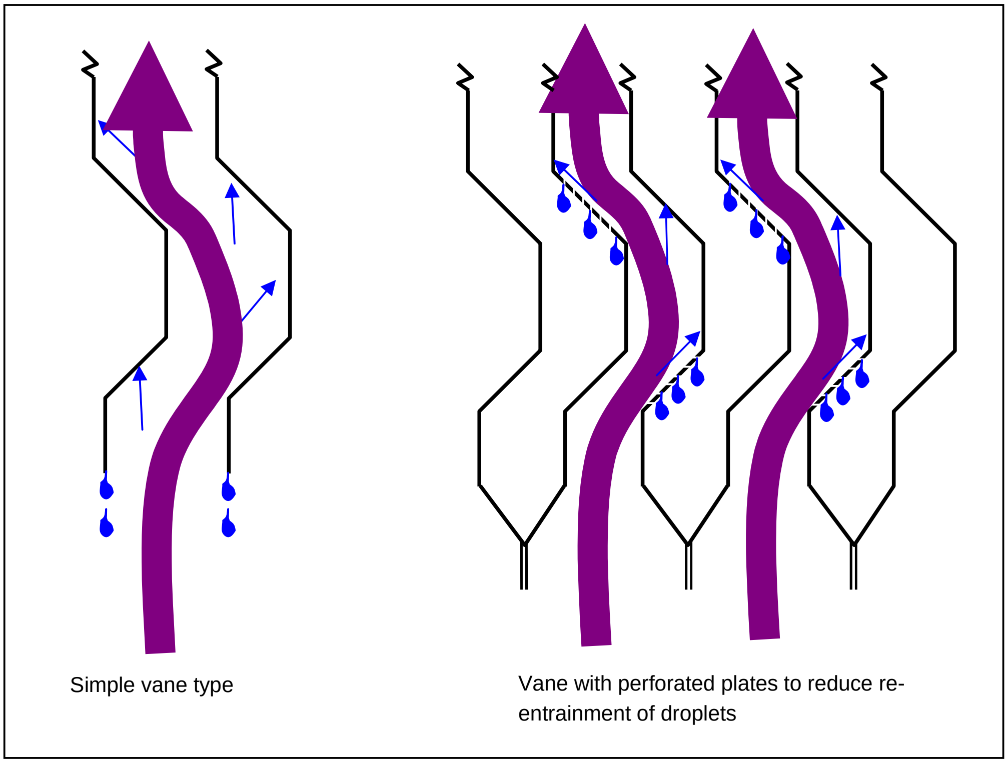


Figure 4.5 Vane type demisters

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[25] "Mist Elimination", Product Catalogue, Koch-Glitsch, 2007

[26] "Measures for Emission Abatement Report", Doc nr. 10112936-FI-A-PRP-0261, Fichtner, 2010

Comparison of mesh- and vane type demisters

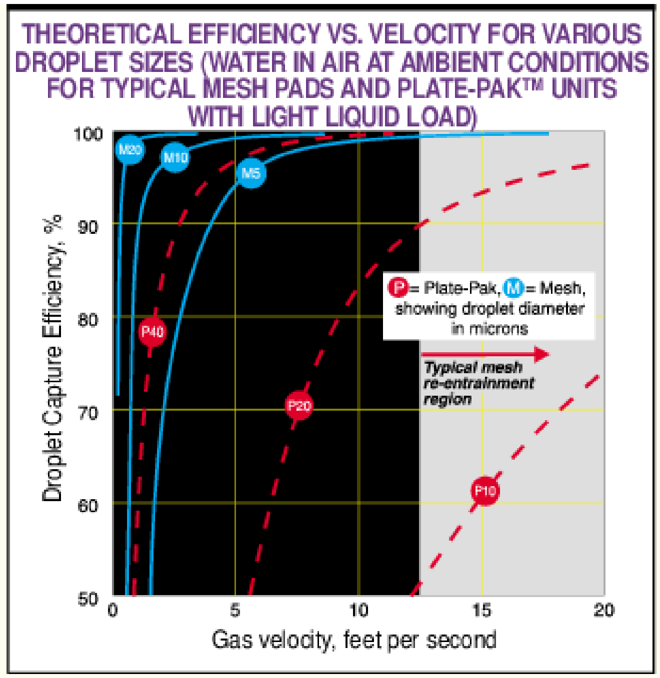

Figure 4.6 Velocity vs. droplet capture efficiency

Velocity is a core element for a demister. As can be seen from figure 4.6 wire mesh demisters can operate in a wider range of velocities than a vane type.[25] These allows for a larger flexibility with respect to utilisation of the power plant.

A mesh pad is the preferred type of demister both based on capture efficiency and allowed velocity range. This is mainly due to the fact that the bending of the gas stream around the fine threads of the mesh pad becomes more sudden than in a vane pack.

4.2.3 Industrial applications

Demisters are utilised in a wide range of applications. Most applications are installed to minimize loss of material, i.e. for economical rather than environmental reasons. It is difficult to find total capture efficiency in the literature, but based on what is described, it is believed that the total capture is measured in the %-scale, not ppm. The droplet size distribution is also not known, so it is difficult to know if the industry applications are relevant for this particular project.

Maturity
Demisters are widely utilised in the industry, and as such regarded as a proven technology. The capture efficiency required in this project however, is not found amongst the installed industry applications. Even if demisters are used in all kinds of industries, literature describing maintenance issues for a demister in a gas fired power plant is not found.

4.2.4 Scale up

The demister is manufactured in sections small enough to be installed through man ways on the column. There is no theoretical maximum size of a demister.

When scaling up a demister, you will have structural issues to take care of. It is also important to ensure optimal gas velocity and an evenly distributed flow over the inlet to the demister.

4.2.5 Energy requirement

A demister is a passive element with no moving parts. Hence, it has no direct energy requirement. Indirectly, because it causes some pressure drop, it is necessary to increase the energy input to the blower on the inlet to the amine contactor. See also chapter 4.2.9 on pressure drop.

4.2.6 Chemical requirement

No chemicals are needed to operate a demister. An occasional cleaning may however be needed, and it that case some chemical use may be necessary.

4.2.7 Size

The height of a demister depends on what type of demister is chosen. In a vertical column, a horizontal demister spanning the entire column area will be in the region 20-30 cm thick. Some void space is needed above and below the demister so a total of 1-1.5 meter should be accounted for.

Increased effect is achieved by installing multiple demisters. The first demister is placed directly after the amine contactor and the others after each water wash section. The different demisters do not have to be equal.

4.2.8 Waste

No waste is produced from normal use of a demister. Based on the type of power plant, contamination and deposits is not expected to pose a problem. What chemicals, if any, that will be used for cleaning is not investigated in this report.

Compared with exhaust from a coal fired power plant, the amount of solids in the exhaust from a gas fired power plant is small. No references for necessary cleaning requirements for a demister with such fine mesh are found. In any case, the necessary cleaning frequency will have to be investigated.

4.2.9 Process implications

Pressure drop

The pressure drop over a demister is low. An exact figure is difficult to provide without intimate knowledge of the application. Different suppliers quote different figures, but a starting point in the region 1-2 mbar is fair estimate applicable for mesh type demisters.

Brownian diffusion candle filters (packed glass fibres) give pressure drop in the region of 20 – 25 mbar, which more than ten times higher than for the knitted mesh type demisters. See also chapter 3.3.

When comparing pressure drops for different suppliers’ technology, it is important to know if the pressure drop is quoted for a wet or a clean demister.

Production stop

For a knitted mesh type demister production stop due to cleaning or maintenance is not believed to be frequent. There are no moving parts in this type demister and there are no solids present in the gas stream. After a test period with checks maybe each 3 months, it is believed that a quick annual or bi-annual check and power hosing is sufficient.

4.3 Functional expectations

For the purpose of defining a qualification basis, a detailed description of the capture plant should form the basis for establishing the functional expectations for the overall process. This description should be clear, comprehensive, accurate and complete. However, the extent to which it can be drawn up before any work is done on the detailed design of equipment will depend on the complexity of the process and the information available (vendor specific and proprietary information), which is likely to reflect the maturity of the process development program, e.g. exploratory research, process research, pilot plant studies or development of a commercial unit. Hence, establishing functional expectations for the CCM capture plant, including the ERTs, can only be based on qualitative requirements.

The overall performance targets for a post-combustion amine CO_2 capture plant is typically related to:

- Capture efficiency (ratio of CO_2 removed from flue gas)
- Energy consumption (MJ/kg CO_2 captured)
- Emissions (ppm levels of solvent)

The different emission reducing technologies relevant for achieving the stated emission targets in this study are likely to cause an increase in cost of capture, both with respect to CAPEX and OPEX, compared to the base case (no ERT). Firstly, a higher absorber will be required in order to fit the additional process equipment and internals within the column. Secondly, an increase in pressure drop and increased flue gas blower duty represents an increased energy cost. Therefore, there is likely to be a trade-off in choosing an ERT, or rather a combination of different ERTs, in order to both minimize emissions and cost of capture. However, this can only to be optimized from cost-benefit analysis when the acceptable emission levels have been established.

As for the purpose of the current assessment, cost issues should therefore not be considered as an evaluation criterion that would disqualify any of the identified ERTs.[27] However, parameters that could influence or alter the performance of the power plant or capture facility need to be identified and assessed with respect to a set of qualification requirements, as listed in table 4.2.

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[27] Although cost issues are not considered as a suited evaluation criterion for the current assessment, it should be noted that all of the functional requirements will indirectly have a cost implication for the capture project.

Table 4.2 Identified functional requirements

Parameter		Description	Functional requirement[28]
Primary requirement	Emission of amines	The main functional requirement of concern for this study is the amine emissions.	The ERT should reduce the emission of amines from the absorber down to level of: i) 0.2 - 1 ppmv ii) 0.01-0.2 ppmv
Other requirements	Energy consumption	The introduction of additional process equipment within the absorber, such as water wash sections or demisters, is likely to affect the total pressure drop over the absorber, and increase the power duty on the flue gas blower. Also, aspects related to water balance for water wash systems will affect the energy consumption of the capture plant. A maximum increase in the total energy penalty for CO_2 capture should be defined. Quantifying acceptance criteria should be based on a technical-economical evaluation of the capture plant, also complying with governing HSE regulations, i.e. amine emission targets.	No significant increase in the total energy requirement of the CO_2 capture plant as a result of the ERT.
	Interface and operational issues	An important interface for CO_2 capture systems is the integration between the capture plant and the power plant. The introduction of ERT within the absorber should not increase the likelihood of any negative influence from the capture	No negative influence on the operation of the power plant caused by the introduction of the ERT.

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[28] Note that the functional requirements (except from the emission targets) are given in a qualitative manner, and acceptable performance targets should be established and agreed upon in collaboration with Contractor at a later stage.

Parameter	Description	Functional requirement[28]
	plant to the gas power plant, such as "back pressure" effects.	
Parameter	**Description**	**Functional requirement14F**
New emissions and waste handling	For ERTs where introduction of chemicals (such as for chemical water wash systems) is needed to achieve the targeted emission levels, all new emissions related to chemical and waste handling should be identified and quantified.	The ERT shall not introduce any new harmful emission or extensive waste treatment.
Reliability, Availability, Maintenance (RAM)	The basic idea of RAM analysis is to analyse how a system performs in its environment including the component failures which can be expected during operation, including maintenance activities. Adding ERTs will increase the complexity of the capture plant, which in turn potentially could influence the reliability of the capture plant. The worst case scenario is that the power plant regularity is affected. However, the most likely consequence of reduced availability of a post-combustion capture plant is that the exhaust gas will be released through the stack.	The ERT shall not have significant negative impact on regularity of CO_2 capture plant or the power plant.
Scalability[29]	The absorber will have a large cross section area and the ERT will be at a scale where there is limited operational history. Hence, scale-up issues is an important parameter when assessing the feasibility of the technology.	The ERT shall have no restrictions (mechanical, structural or functional) with respect to scale-up.

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[29] Note that scale-up issues are treated separately in chapter 4.4, as a part of the maturity evaluation

4.4 Maturity assessment

4.4.1 The Technology Readiness Level (TRL)

One assessment method which can be used to underpin the qualification process is the TRL, which indicates the extent to which an item is "ready for use" given specified qualification factors/requirements. The TRL approach focuses on previous experience and track-record of the technology.

In API RP 17n, eight TRLs have been defined ranging from a minimum of 0, corresponding to an unproven idea, to a maximum of 7, corresponding to proven technology (installed and operating in the relevant conditions). These are shown in table 4.3.

Water wash
Industrial application is considered similar to the application of chemical absorption processes (amine plants), and a summary of relevant commercial and pilot plants are listed in appendix 2. Thus, the water-wash technology is in general considered a proven technology for removing CO_2 from hydrocarbon gases. Most applications are installed to minimize loss of material, i.e. for economical rather than environmental reasons.

For the required scale and emission levels relevant for CCS, no track record is known to exist, neither are full scale prototypes. Several companies and R&D centres have pilot scale absorber units with water wash in operation (a list of commercial and pilot CO_2 capture plants can be found in appendix 2). Hence, this technology can be regarded as having a TRL value of 3.

Chemical wash
Chemical wash (acid wash) can be regarded as a special case of water wash. Chemical wash is most probably tested in some of the pilot scale absorbers in operation, but the extent of testing is not known due to proprietary technology. This technology can therefore be regarded as having a TRL value of 2 or 3. Acid wash has been considered being less mature than water wash, and as a consequence the Technology Readiness Level has been rated lower.

Demisters
Demisters (mesh and vane types) are utilised in a wide range of applications. Most applications are installed to minimize loss of material, i.e. for economical rather than environmental reasons. For the required scale and emission levels, no track record is known to exist, neither are full scale prototypes. Several companies and R&D centres have pilot scale absorber units with demisters in operation. (A list of commercial and pilot CO_2 capture plants can be found in Appendix 2). Hence, this technology can be regarded as having a TRL value of 3.

Table 4.3 Definition of Technology Readiness Levels (TRLs) (from API RP 17n)

	TRL	Development Stage Completed	Definition of Development Stage
Concept	0	**Unproven Concept** (Basic R&D, paper concept)	Basic scientific/engineering principles observed and reported; paper concept; no analysis or testing completed; no design history
Proof of Concept	1	**Proven Concept** (Proof of concept as a paper study or R&D experiments)	a) Technology concept and/or application formulated b) Concept and functionality proven by analysis or reference to features common with/ to existing technology No design history; essentially a paper study not involving physical models but may include R&D experimentation
	2	**Validated Concept** Experimental proof of concept using physical model tests	Concept design or novel features of design is validated by a physical model, a system mock up or dummy and functionally tested in a laboratory environment; no design history; no environmental tests; materials testing and reliability testing is performed on key parts or components in a testing laboratory prior to prototype construction
Prototype	3	**Prototype Tested** (System function, performance and reliability tested)	a) Item prototype is built and put through (generic) functional and performance tests; reliability tests are performed including; reliability growth tests, accelerated life tests and robust design development test program in relevant laboratory testing environments; tests are carried out without integration into a broader system b) The extent to which application requirements are met are assessed and potential benefits and risks are demonstrated
	4	**Environment Tested** (Pre-production system environment tested)	Meets all requirements of TRL 3; designed and built as production unit (or full scale prototype) and put through its qualification program in simulated environment (e.g. hyperbaric chamber to simulate pressure) or actual intended environment (e.g. subsea environment) but not installed or operating; reliability testing limited to demonstrating that prototype function and performance criteria can be met in the intended operating condition and external environment
	5	**System Tested** (Production system interface tested)	Meets all the requirements of TRL 4; designed and built as production unit (or full scale prototype) and integrated into intended operating system with full interface and functional test but outside the intended field environment
Field Qualified	6	**System Installed** (Production system installed and tested)	Meets all the requirements of TRL 5; production unit (or full scale prototype) built and integrated into the intended operating system; full interface and function test program performed in the intended (or closely simulated) environment and operated for less than 3 years; at TRL 6 new technology equipment might require additional support for the first 12 to 18 months
	7	**Field Proven** (Production system field proven)	Production unit integrated into intended operating system, installed and operating for more than three years with acceptable reliability, demonstrating low risk of early life failures in the field

4.4.2 The Technology Classification principle

The Technology Classification principle is outlined in DNV-RP-A203 and DNV-RP-J201, and comprises a Technology Assessment. The purpose of the Technology Assessment is to break down the technology into manageable elements, assess which elements that involve new technical aspects and identify the key challenges and uncertainties.

The Technology Classification principle enables identifying future needs for qualification in order to mature a concept.

4.4.3 Technology Breakdown

Amine recovery systems are an integral part of a CO_2 absorber. The purpose of the current project is to assess and compare different technologies for amine recovery. Combined with the limited detail level of the considered technologies, a further breakdown of the amine recovery assembly has not been considered relevant.

4.4.4 Technology Classification

The classification was performed in a workshop involving participants from DNV and SINTEF. The assessment was performed according to DNV-RP-J201, ref. table 4.4.

Table 4.4 Classification of Technology classes according to DNV-RP-A203

Experience with the Operating Condition	**Level of Technology Maturity**		
	Proven	Limited field history or not used by company/ user	New or unproven
Previous experience	1	2	3
No experience by company/ user	2	3	4
No industrial experience	3	4	4

The Technology Classification ratings are defined as follows:

1. Proven technology - No new technical uncertainties
2. New technical uncertainties
3. New technical challenges
4. Demanding new technical challenges

The objective of this exercise is to highlight the areas where care must be taken during the design and qualification process due to new technological elements, new application areas for existing/known technology and/or limited field history.

Technology in class 1 is proven technology where proven methods for qualification, tests, load and structural analysis can be used to document margins to failure. It is assumed that acceptable margins to failure for these items are achieved through the regular project activities in order to ensure a reliable qualification process for the components in this technology class.

Technology defined as class 2 to 4 is defined as new technology, and requires qualification according to DNV-RP-A203/ DNV-RP-J201 or equivalent. Components assigned to these classes will later be subject to Failure Mode Identification and Risk Ranking. For sub-components that fall into class 2 to 4, further subdivision of these components may be necessary based on the Failure Mode Ranking process and the complexity of the sub-components.

The main challenge for components with proven technology that are to be used in new application areas will be to identify the difference between the known and the new application areas, and then document the margins to failure to cover the uncertainties introduced by the new application.

4.4.5 Main results of the Technology Assessment

The main results from the Technology Assessment consist of a spreadsheet from a workshop held with participants from DNV and SINTEF on 16th September, see appendix 1. The spreadsheet comprises the Technology Classification, new aspects, critical parameters, main challenges/uncertainties and advantages for the different technologies considered. The results from the Technology Classification are shown in table 4.5.

Table 4.5 Classification of the different technologies considered

Technology	Class
Water wash, Solvent A	3
Water wash, Solvent B	4
Demister, Mesh type	3
Demister, Vane type	3

Both water wash with Solvent A and the two demister technologies were considered proven technologies, while Water wash with Solvent B has limited field history. (See table 4.4). However, at the relevant operating conditions there exists no industrial experience for any of the technologies.

Chemical wash (acid wash) can be regarded as a special case of water wash. Limited industrial experience results in a class 4 for chemical wash.

The new aspects that were identified are summarised in table 4.6. Some of the main challenges and uncertainties related to the new aspects were identified, and includes:

- Droplet concentration and size distribution of the droplets are not known
- Penetrating droplets of size 0.2 to 1 μm might reach significant concentrations
- Measurement methods are not available for all degradation products. No standardised measurement methods are available, neither for degradation products nor for amines at the required low concentrations.
- The water balance (relevant for water wash systems) is partly controlled by the temperature in the water wash section, and has to be optimised, both with respect to flue gas buoyancy issues and amine evaporation.

Table 4.6 New aspects

Technology	**New aspects**			
	Large scale	**Inlet gas composition**	**Amine recovery level**	**Solvent**
Water wash, Solvent A	X	X	X	–
Water wash, Solvent B	X	X	X	X
Demister, Mesh type	X	X	X	n/a
Demister, Vane type	X	X	X	n/a

4.5 Technology performance assessment

4.5.1 Description of ERTs

The relevant technologies are water wash, chemical wash and demister systems as described in chapter 4.1 and 4.2. Available information on lesser known ERT for application in amine based CO2 capture plants has been insufficient for performance and maturity evaluations based on DNV methodology

It should be noted that the descriptions of technologies have been made on a generic basis as specific information on configuration aspect (e.g. placement of internals) of process units and internals from reference plants or vendor specific plants are not available in the open literature. Hence, the subsequent assessment of the ERTs is based on information within the project team and publicly available information.

4.5.2 Benchmarking of ERTs

Methodology

The ERTs that are considered to be the most mature have been assessed with respect to how likely they are to meet the functional expectations established in chapter 4.3. As a generic absorber design is used, and no testing has been performed on the ERTs, only a qualitative benchmarking exercise is carried out using traffic lights (red/yellow/green) defined as follows:

🔴	Not likely to meet functional expectations
🟡	Functional expectation may or may not be met (unable to assess based on a generic design)
🟢	Likely to meet functional expectations

The assigned traffic lights indicate to what extent an ERT is able to meet the functional expectations to the technology, listed in table 4.2. Hence, the traffic light assessment should be regarded as a tool for assessing and comparing the relative expected performance between the ERTs.

Basis and assumptions

Demisters and water wash are discussed in the previous sections as two emission reducing technologies that will reduce amine concentration in the vapour phase and in entrained droplets, respectively. In addition to these technologies it is foreseen, based on chemical engineering judgement, that a lowered pH in the water wash would enhance the capture efficiency of any alkaline amine solvent. The concept of chemical/acid wash, when compared to demisters and water wash, is not considered mature enough for any benchmarking exercise, however, it is included in the current assessment as a special version of water wash. The following assumptions apply for the performance expectation assessment:

- It is assumed that the basis absorber configuration will be equipped with two demisters; one at the inlet of the ERT section (after the absorption section) and one at the outlet of the absorber tower (after the ERT)
- It is not distinguished between the different types of demisters that could be deployed
- The assessment has been restricted to maximum two washing sections
- Acid wash is only considered as a final “polishing stage” in combination with a water wash section.
- Effects of submicron aerosols and foam formation are unknown but is handled to be negligible in order to complete these assessment

Table 4.7 Traffic light assessment of ERTs for solvent A

Alternatives for emission reducing units	Amine Emissions		Energy Consumption		Interface and operational issues	New emissions and waste handling	Reliability, Availability, Maintenance (RAM)	Scalability
	<1 ppmv	<0.2 ppmv	<1 ppmv	<0.2 ppmv				
One water wash section and demisters	🟢	🔴	🟢	🟡	🟢	🟢	🟢	🟡
Two water wash sections and demisters	🟢	🟡	🟢	🟡	🟢	🟢	🟢	🟡
One water wash section, one acid wash section and demisters	🟢	🟡	🟡	🟡	🟢	🟡	🟢	🟡

Table 4.8 Traffic light assessment of ERTs for solvent B

Alternatives for emission reducing units	Amine Emissions		Energy Consumption		Interface and operational issues	New emissions and waste handling	Reliability, Availability, Maintenance (RAM)	Scalability
	<1 ppmv	<0.2 ppmv	<1 ppmv	<0.2 ppmv				
One water wash section and demisters	🔴	🔴	🟡	🟡	🟢	🟢	🟢	🟡
Two water wash sections and demisters	🟡	🔴	🟡	🟡	🟢	🟢	🟢	🟡
One water wash section, one acid wash section and demisters	🟡	🔴	🟡	🟡	🟢	🟡	🟢	🟡

Table 4.7 and table 4.8 show the assessment for solvent A and solvent B, respectively. From table 4.7 it can be seen that the emission target of less than 1 ppmv amine is likely to be met using just one water wash section for solvent A, whereas at least two water wash sections are needed to approach the lower limit of less than 0.2 ppmv. However, even for two washing sections it is still uncertain to what extent the targeted concentration levels can be reached. Real emission data, e.g. from piloting, will be needed in order to provide confidence in capture efficiency of such systems. Even piloting can not provide "real emission data", mainly because long term accumulation of degradation products in the adsorbent would be different. To a large extent this difference might govern how representative data from a pilot plant becomes relative to a full scale plant.

When it comes to energy consumption it is evident that the different amine emission targets will influence the energy consumption, as extra make-up water will be require to obtain targeted recovery level and this is likely to increase the re-boiler duty. Also, a chemical wash with acids will cause an increased load on the waste handling system of the capture plant. However, it is difficult to assess the extent of this as these systems are very immature and limited public information is available.

It is not foreseen that the introduction of the ERTs, independent of solvent type, listed in the tables above, will cause additional operational problems or decreased availability for the power plant. Moreover, the scalability of the ERTs is not likely to differ from the rest of the absorber column internals (e.g. packing materials, gas and liquid distributors) and qualification activities are needed in order to provide confidence in the technology at full commercial scale.

The same rationale for assessing solvent A is valid for solvent B, listed in Table 4.8. However, solvent A is more easily absorbed with CO_2 in water compared to solvent B, as solvent B is likely to be more volatile than solvent A. This implies a poorer performance in terms of capture efficiency by the water wash section and also probably slightly higher energy consumption for solvent B.

The maturity assessment and benchmarking of water wash, chemical wash and demister systems applied in amine based CO2 capture plants have been performed using systematic DNV methodology. Available information on lesser known ERT for application in such CO_2 capture plants has been insufficient for performance and maturity evaluations based on DNV methodology.

5. CONCLUSION AND RECOMMENDATIONS

Dissolved in water AMP is more volatile than MEA, because of the large solubility of MEA in water compared to AMP. In addition MEA vapour from solvent A is more easily absorbed with CO_2 in water compared to the AMP vapour from solvent B. These two favourable characteristics of solvent A give lower amine emission from the CO_2 absorber and also better separation efficiency by the water wash sections.

The emission target of less than 1 ppmv amine is likely to be met with one water wash section for solvent A, whereas at least two water wash sections are needed to approach the lower limit of less than 0.2 ppmv. Even for two washing sections it is still uncertain to what extent the targeted concentration levels can be reached.

The simulations do not include any liquid entrainment. Amount of aerosol formation in the absorber and its penetration through water wash sections including the demisters can not be calculated.

Liquid water content of fog (LWC) is typical 50 mg/Nm^3 dry air. If such a concentration of liquid aerosol also appear in gas outlet from the absorption column containing 12 vol. % water vapour and the droplets contain 10 wt % of MEA, then the corresponding concentration of liquid MEA in the gas becomes1.6 ppm. Fog formation and outlet concentration of dispersed droplets depends very much on process conditions. Reliable droplet concentration levels and amine content in such droplets should be demonstrated by pertinent and thoroughly performed laboratory and pilot experiments.

It is not be unreasonable conservative to assume that MEA in the aerosol emission from a new plant can contribute in the order of 0.1 – 0.2 ppm MEA to the total emission of MEA even after two stages of water wash including demisters. However, in the absence of experimental data or a model it is difficult to come up with a scientific justification of this assumption.

Only pertinent and thoroughly performed laboratory and pilot experiments might demonstrate reliable emission levels of nitrosamines and nitramines. If it is found that these emission levels are too high, we would recommend the use of UV-light in combination with water-wash and acid-wash. The simplest use of UV-light would be treating the liquid phases in the water-wash and/or acid-wash and thereby reverse the formation of nitrosamines and/or nitramines. If the acid wash and UV-treatment is integrated properly, almost all potential nitrosamines, nitramines and nitrosamine/nitramine precursors could be captured in the acid-wash (the UV reversing the nitrosamines and nitramines to amines that will bind in an acid wash). The more demanding option would be to use UV light to treat the flue gas coming through the water wash. The main issue may be the residence time needed for a UV process.

Further research and investigations are needed in order to improve the reliability of the conclusions in this report. We recommend main efforts to be put on the following subjects in the extended work:

1. Evaluation and selection of test facilities

2. Evaluation and selection of emission measurements methods

3. Emission measurements from absorber demister units and water wash sections in test facilities including pilot plants. Measurements includes sampling and analysis of total amine content in gas flow including degradation products

4. Verification and measurement of fog formation including qualitative continuous registration of mist and fog

5. Validation of simulation results from CO2SIM

6. Validation of gas liquid equilibrium data on very low partial pressure

7. Sampling and analysis of non-volatile tracers added to the absorbent solution in order to validate droplet entrainment from absorber solution

8. Sampling and analysis of non-volatile tracers added to the first water wash stage in order to validate droplet entrainment from water wash solution

9. Gathering of data from industrial plants

Appendix 1

Results from the Technology Assessment workshop, 2010-09-16

Results from the Technology Assessment workshop, 2010-09-16

ID	Technology Description	New Aspects	Critical parameters/issues	Operating Condition	Maturity	Tech. Class	Main challenges and uncertainties	Advantages	Comments
1	**Water wash (Solvent A)**	No experience at this scale		3 - No industry experience	1 - Proven	3			Extensive industrial experience with water wash of Solvent A (MEA), but at smaller scale
		Inlet gas composition (exhaust)					Droplet concentration and size distribution of the droplet are not known		Technology is used for exhaust gas at smaller scale and only for different applications. Absorption of amine degradation products will occur but is not well known.
		Purification level of 0.1 - 1 ppm exit concentration of sum toxic compounds from amines and degradation products in aerosols and of vapours					Penetrating droplets of size 0.2 to 1 µm might reach significant concentrations	If CO_2 saturated water is used, CO_2 will bind amines.	Solvent A (MEA) is more easily absorbed with CO_2 in water. This effect is not significant for Solvent B.
							Measurement methods for amines and degradation products		Measurement methods are not available for all degradation products. No standardised measurement methods are available, neither for degradation products nor for amines at the required low concentrations. This will of course apply to all technologies.

ID	Technology Description	New Aspects	Critical parameters/issues	Operating Condition	Maturity	Tech. Class	Main challenges and uncertainties	Advantages	Comments
							Foaming in absorber unit		Affects emitted concentrations of toxic compoundsl
							Number of washing steps, which will influence height, is not known		Number of washing steps dependens on emission limit requirements, washing step performance and temperature. Number of steps and performance will influence tower height
		Large scale	Scale up				Liquid distribution uncertain		Design method for effective distribution not well known for this scale.
							Design of combined methods for CO_2 absorption and amine recovery in the first washing step is not defined		
			Energy req.						Pumping of liquid in each washing step. Gas pressure loss across washing sections is approximately 200 Pa per meter of packing elements. Pressure drop across demister is approx. 100-200 Pa for each washing step. If extra make up water is needed (to obtain required recovery level), this may increase the energy consumption in the reboiler.

ID	Technology Description	New Aspects	Critical parameters/issues	Operating Condition	Maturity	Tech. Class	Main challenges and uncertainties	Advantages	Comments
									Strict regulation regarding water effluent quality may also increase energy demand.
			Chemical req.					No chemicals needed	With chemical wash the acid outlet water can not be recirculated to the absorber. Separate treatment is needed. Chemical washing is regarded as the last, supplementing step to achieve required recovery. (Only used if necessary)
			Waste					Degradation products are not likely to be formed by water washing	Water can be treated with UV light before recirculation. Increased retention time may increase degradation. Material selection is essential for avoiding degradation of amines.
			Process implication				Water cycle		
							Temperature		Gas inlet temperature may influence evaporation in amine plant. May influence water consumption. If process has to be run at low temperature to reach spec. this may result in a larger column
									The higher the outlet temperature, the more water mist out, but better plume

ID	Technology Description	New Aspects	Critical parameters/issues	Operating Condition	Maturity	Tech. Class	Main challenges and uncertainties	Advantages	Comments
									dispersion.
			Materials				Corrosion		Material selection is essential for avoiding degradation of amines. Corrosion products can catalyse amine degradation
2	**Water wash (Solvent B)**	No experience at this scale		3 - No industry experience	2 - Limited history	4			Limited experience with water washing of AMP (Solvent B), and only at smaller scale
		Inlet gas composition (exhaust) at large scale					Droplet concentration and size distribution of the droplet are not known		Technology is used for exhaust gas at smaller scale and only for different applications. Absorption of amine degradation products will occur but is not well known.
		Amine recovery level					Penetrating droplets of size 0.2 to 1 µm might reach significant concentrations	If CO_2 saturated water is used, CO_2 will bind amines.	MEA (Solvent A) is more easily absorbed with CO_2 in water. This effect is not significant for Solvent B (AMP). AMP is more volatile than MEA. Measurement methods are not available for all degradation products. (Applies to all technologies and also to amine concentration at the required low levels.) No standardised methods.

ID	Technology Description	New Aspects	Critical parameters/issues	Operating Condition	Maturity	Tech. Class	Main challenges and uncertainties	Advantages	Comments
							Measurement methods for amines and degradation products		Measurement methods are not available for all degradation products. No standardised measurement methods are available, neither for degradation products nor for amines at the required low concentrations. This will of course apply to all technologies.
							High amine concentration from the absorber		3-5 times higher with Solvent B than with Solvent A.
							Foaming in absorber unit		Affects emitted concentrations of toxic compounds
							Number of washing steps, which will influence height, is not known		Number of washing steps dependens on emission limit requirements, washing step performance and temperature. Number of steps and performance will influence tower height
							Design of combined methods for CO_2 absorption and amine recovery in the first washing step is not defined		
		Large scale	Scale up				Liquid distribution uncertain		Design method for effective distribution not well known for this scale.

ID	Technology Description	New Aspects	Critical parameters/issues	Operating Condition	Maturity	Tech. Class	Main challenges and uncertainties	Advantages	Comments
			Size and weight				More washing steps may be required with Solvent B than with Solvent A		
			Energy req.						Pumping of liquid in each washing step. Gas pressure loss across washing sections is approximately 200 Pa per meter of packing elements. Pressure drop across demister is approx. 100-200 Pa for each washings step. If extra make up water is needed (to obtain required recovery level), this may increase the energy consumption in the reboiler. Strict regulation regarding water effluent quality may also increase energy demand.
			Chemical req.					No chemicals needed	With chemical wash the acid outlet water can not be recirculated to the absorber. Separate treatment is needed. Chemical washing is regarded as the last, supplementing step to achieve required recovery. (Only used if necessary)

ID	Technology Description	New Aspects	Critical parameters/issues	Operating Condition	Maturity	Tech. Class	Main challenges and uncertainties	Advantages	Comments
			Waste					Degradation products are not likely to be formed by water washing	Water can be treated with UV light before recirculation. Increased retention time may increase degradation. Material selection is essential for avoiding degradation of amines.
			Process implication				Water cycle		
							Temperature		Gas inlet temperature may influence evaporation in amine plant. May influence water consumption. If process has to be run at low temperature to reach spec. this may mean a larger column
									The higher the outlet temperature, the more water mist out, but better the plume dispersion.
			Materials				Corrosion		Material selection is essential for avoiding degradation of amines. Corrosion products can catalyse amine degradation. Effects are less known for Solvent B than for Solvent A . The corrosion problem is similar for the absorber and the washing.
3	**Demister, Wire mesh type (horizontal)**	No experience at this scale		3 - No industry experience	1 - Proven	3	Wire mesh demisters are not well known in this scale.	Scale up is considered easier than for water wash	Vane demisters are more used at larger scale (coal fired power plants).

ID	Technology Description	New Aspects	Critical parameters/issues	Operating Condition	Maturity	Tech. Class	Main challenges and uncertainties	Advantages	Comments
								More experience with wire mesh demisters than with vane demisters for capture of droplets of size 2 - 100 µm	
		Purification level of 0.1 - 1 ppm exit concentration of sum toxic compounds from amines and degradation products in aerosols and of vapours							Required recovery level is orders of magnitude lower than for commercial technology
							Fraction of sub micron droplets (<1µm) is not known	Coalescer effect	Coalescer effect of small threads - may increase droplet size
							The gas coming out of the amine absorber may contain impurities		Whether these will affect the performance of the demister over time or not must be investigated
			Size and weight					Scale up is easier than for water wash	Gas velocity constraints implies large area requirements. Several demister steps will be required. E.g. before and after water washing steps.

ID	Technology Description	New Aspects	Critical parameters/issues	Operating Condition	Maturity	Tech. Class	Main challenges and uncertainties	Advantages	Comments
			Energy req.					Low pressure drop	
			Chemical req.					None	
			Waste						As for water wash
			Process implication						Pressure drop across wire mesh demisters is normally lower than for vane type. Capture of sub micron droplets implies depth filtration through packed glas fibres and much larger pressure drop
			Gas velocity						Too high gas velocity will cause droplets to be carried away.
			Materials						Avoid water repellent materials
4	**Demister, Vane type**	Limited experience at this scale		3 - No industry experience	1 - Proven	3		Scale up is easier than for water wash	Maybe three times as large as for coal fired power plants.
		Purification level of 0.1 - 1 ppm exit concentration of sum toxic compounds from amines and degradation products in aerosols and of vapours					Penetrating droplets of size 0.2 to 1 µm might reach significant concentrations		Required limits of emitted concentrations is orders of magnitude lower than obtained by commercial technology

ID	Technology Description	New Aspects	Critical parameters/issues	Operating Condition	Maturity	Tech. Class	Main challenges and uncertainties	Advantages	Comments
							Fraction of sub micron droplets is not known	Coalescer effect	Coalescer effect of small threads - may increase droplet size
							The gas coming out of the amine absorber may contain impurities		Whether these will affect the performance of the demister over time or not must be investigated
			Size and weight						Several demister steps will be required. E.g. before and after water washing steps.
			Energy req.						Pressure drop is larger than for wire mesh demisters
			Chemical req.					None	
			Waste						As for water wash
			Process implication						Capture of sub micron droplets implies larger pressure drop.
			Gas velocity				Will require specific gas velocity		Vane demisters are more sensitive to gas velocity variations than wire mesh demisters
			Materials						Avoid water repellent materials

Appendix 2

Survey of amine based carbon capture facilities

Survey of amine based carbon capture facilities

Fluor

OWNER	LOCATION	SIZE, Te/D	CO2 USE
Plants no longer in operation			
N-Ren Southwest	Carlsbad, New Mexico	90	EOR
Carbon Dioxide Tech. Corp.	Lubbock, Texas	1000	EOR
Paca	Israel	25	Food Industry
Plants in operation			
Liquid Air Australia	Altona, Australia	60	Food Industry
Liquid Air Australia	Botany, Australia	60	Food Industry
*Industrial de Gaseoses Cia. Ltda	Quito, Ecuador	6.0	Food Industry
*Pepsi Cola	Manila, Philippines	6.0	Food Industry
*Pepsi Cola	Quezon City, Philippines	6.0	Food Industry
*Cosmos Bottling Co	San Fernando, Philippines	6.0	Food Industry
*San Miguel Corp	San Fernando, Philippines	45	Food Industry
Indo Gulf Fertilizer Co	Uttar Pradesh, India	150	Urea Plant Feed
Luzhou Natural Gas	Sechuan Province, PRC	160	Urea Plant Feed
Northeast Energy Associates	Bellingham, Mass	320	Food Industry
Kansei Electric Power Co.	Osaka, Japan	2.0	Pilot Plant
Tokyo Electric Power Co.	Japan	5.0	Pilot Plant
Sumitomo Chem/Nippon Oxygen	Chiba, Japan	160	Food Industry
*Cervezaria Baveria	Barranquilla, Colombia	25	Food Industry
Prosint	Rio de Janeiro, Brazil	90	Food Industry
*Coca Cola	Cairo, Egypt	6.0	Food Industry
*Azucar Liquida SA	Santo Domingo, Dom. Rep	6.0	Food Industry
# European Drinks	Sudrigiu, Bihor County Romania	36	Food Industry
* Messer Greisheim do Brazil Ltda	Sao Paulo, Brazil	50	Food Industry
# Messer Greisheim do Brazil Ltda	Sao Paulo, Brazil	80	Food Industry

Mitsubishi

OWNER	LOCATION	SIZE, metric T/D	CO2 USE
Petronas Fertilizer(Kedah) Sdn Bhd	Kedah Darul Aman, Malaysia	160 (Max. 200)	Urea production
'A' chemical company	Fukuoka, Japan	283 (Max 330)	General use (Several Industries)
Indian Farmers Fertiliser Co-Operative Ltd.	Aonla, India	450	Urea Production
Indian Farmers Fertiliser Co-Operative Ltd.	Phulpur, India	450	Urea Production
Nagarjuna Fertilizers and Chemicals Limited	Kakinada, India	450	Urea Production
Ruwais Fertilizer Industries	Abu Dhabi , United Arab Emirates	400	Urea Production
Gulf Petrochemical Industries Co.	Bahrain	450	Urea Production
Engro Fertilizers Limited	District Ghotoki, Pakistan	340	Urea Production
Petrovietnam Fertilizer and Chemicals Corporation	Phu My, Vietnam	240	Urea Production

Kerr-McGee/ABB Lummus

OWNER	LOCATION	SIZE, metric T/D	CO2 USE
North American Chemical Corp.	Argus Soda Ash facility in Trona, California	800	Brine carbonation
Kerr-McGee/Lummus Crest	Oklahoma	200	Food grade
Soda Ash Botswana, (Pry.) Ltd.'s	Botswana?	300	Soda ash

Pilot plants

OWNER	LOCATION	SIZE, metric kg/h	Type of Facility & Use of CO2
SINTEF+NTNU	Trondheim, Norway	10	Flue gas from a propane burner may be used to generate natural gas or coal derived flue gas quality. May be used for testing of new absorbents
Dong Energy, Vattenfall – Castor	Esbjerg, Danmark	1000	Connected to a coal fired power station. Used for research purposes, with MEA and new solvents in the EU projects CASTOR and CESAR
RWE/BASF/Linde	Nideraußem, Tyskland	300	Connected to a lignite fired power station. Intended for studies of "all aspects of CO_2 scrubbing"
RWE power	Didcot, UK	42	Connected to a coal fired power station. Post combustion and oxyfuel Absorbent: amines of unspecified type
Aberthaw Power Station	UK	2083	Under construction, expected finished in 2013. Connected to a coal fired power station. Combined CO_2- and SO2-capture
University of Texas	Texas, USA	200	Packing material: Flexipac-1Y/IMTP40 are mentioned, but the facility does not appear to be limited to these types.
DOE Center	Wilsonville Alabama, USA		Intended to handle flue gases form coal, biofuel as well as from other types of fuel. Wide selection of parallel rigs pre- and postcombustion "Current participants in the NCCC project include American Electric Power, Luminant, the Electric Power Research Institute, Arch Coal, Peabody Energy, and RioTinto".
Powerspan First Energy Corps,	Shadyside Ohio, USA	835	Burger Plant, Uses ammonia instead of amines. Connected to a coal fired power station
International test centre (ITC) for CO_2 Capture	University of Regina, Canada	167 (+ one smaller)	The absorbents studied comprise at least MEA and mixtures of MEA and MDEA.
Huaneng	Peking, China	500	Connected to a coal fired power plant
Huaneng	Shanghai, China	10 000 t/yr	Connected to a coal fired power plant
CSIRO	Newcastle, Australia	100 000 t/yr	Connected to a coal fired power plant. Mobile rig. Designed for flexibility with regard to absorbents

Appendix 3 Biological treatment of amine-containing exhaust – A short outline of possibilities

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Biotreatments of amine-containing exhaust air – a short outline of possibilities

Kjell D. Josefsen, Dept. of Biotechnology, SINTEF Materials and Chemistry

TABLE OF CONTENTS

1 ABSTRACT

Applied biological waste gas purification technology currently includes biofilters, biotrickling filters and bioscrubbers. In all systems gas containing volatile compounds is passed through the bioreactor where the volatile compounds are transferred from the gas phase into the liquid phase. Microorganisms growing in the liquid phase, usually as a biofilm on the carrier material, degrade the compounds dissolved in the liquid phase. The microbial community responsible for the biodegradation normally consists of a mixture of different bacteria, fungi, and protozoa. Often the waste gas contains many different chemical compounds. The remarkable aspect of the microbial community is that it generally develops to a composition so that all the different chemicals are removed and metabolized simultaneously.

Biological waste gas treatment is a possible secondary treatment after water scrubbing of the waste gas from the amine-based CO_2 capture unit. However, the amount of gas to be treated is roughly an order of magnitude larger than what is treated in the largest existing plants. A bioscrubber appears to be the most interesting biofilter system due to the high solubility of most of the pollutants (amines). An alternative to a bioscrubber could be a second water scrubber. Because the design of the bioscrubber must take into account the formation of biofilm, the absorption process will probably be a less efficient than in a water scrubber. On the other hand, a bioscrubber may employ recycled wastewater and thus not increase the volume of wastewater to be handled.

Further studies are required to reach a final conclusion, but since most of the pollutants from the amine-based CO_2 capture unit are highly water soluble and has alkaline properties, a water/acid wash may be a better option than a bioscrubber. The subsequent treatment of the generated wastewater to remove the dissolved compounds should, however, be biological.

2 BACKGROUND

2.1 Emissions from amine based carbon capture

An amine-based CO_2 capture process is considered to capture approx. 1.3 million tons CO_2 per year released from a combined heat and power plant at Mongstad. This CO_2 capture process will release potentially harmful substances to the atmosphere, notably small amounts of the employed amines as well as degradations products of these compounds, including carcinogenic nitrosamines. The exhaust gas will therefore have to be treated before it is released to the surroundings. In this report the use of biological treatment technologies are considered.

2.2 Biological waste gas treatment

Several different technological designs have been developed that use microorganisms to remove substances from waste gas. The technique is used by industries producing food and animal products, pharmaceuticals, wood products, paint and coatings, and resins, as well as to treat off-gas from wastewater treatment facilities and livestock facilities. Compounds treated are typically mixed volatile organic compounds and various sulfur compounds, including hydrogen sulfide (H_2S). Units treating gas flows of up to at least 150 000 m^3 per hour have been constructed.

2.3 Gas volumes and content

For calculation purposes a gas volume of 10^6 m^3 per hour is used. When the gas leaves the CO_2 capture unit it is assumed to contain 100 mg monoethanolamine (MEA) or 250 mg aminomethyl-propanol (AMP) per cubic meter (depending on the type of amine used for CO_2 capture). In addition comes roughly 500 mg/m^3 ammonia (NH_3) and probably small amounts of various degradation products. The first exhaust gas treatment is assumed to be a “water wash” that will reduce the content with more than 90 %. Biological gas treatment will most likely be a secondary treatment using the exhaust gas from the “water wash unit”. This gas is for calculation purposes assumed to contain approximately 3 mg/m^3 MEA or AMP, and 30 mg/m^3 NH_3. Because of the large gas volumes, this corresponds to 3 kg MEA/AMP and 30 kg NH_3 per hour, or roughly 220 ton amino-N per year. For comparison, 10-13 ton N as inorganic fertilizer was used in 1999 per km^2 in Norway for production of wheat and barley (Briseid *et al.*, 2008).

3 THE BIOLOGICAL BASIS

3.1 General

All biological treatment processes are based on microbial degradation of the waste compounds to carbon dioxide, water and inorganic compounds such as ammonia, sulfate and phosphate. In addition microbial biomass is produced. Often the waste to be treated contain many different chemicals, in some cases several hundreds. The great advantage of biological systems is that they usually over some time develop a composition of microorganisms so that so that all the different compounds are removed and metabolized simultaneously.

3.2 Biodegradation of monoethanolamine (MEA)

Most studies indicate that MEA is easily degraded by bacteria both aerobically and anaerobically (Ndegwa *et al*., 2004; Wong *et al*., 2004; Li, 2008). MEA is a constituent of phospholipids and we would therefore expect it to be easily biodegraded. However, a study from an old industrial site in USA (Hawthorne *et al*., 2005) indicates that MEA in some cases can persist in the soil for years. The reason for this is not clear, but may be related to a strong binding of the positively charged MEA to negatively charged soil particles.

If we assume that 50 % of the carbon in MEA goes to biomass and 50 % to CO_2, a theoretical mass balance is:

$$H_2NCH_2CH_2OH + 2.05\ O_2 \rightarrow CH_{1.8}O_{0.5}N_{0.2}\ \text{(biomass)} + CO_2 + 2.6\ H_2O + 0.8\ NH_3$$

or: 1.00 kg MEA + 1.08 kg O_2 → 0.40 kg cell mass (d.w.) + 0.22 kg NH_3 + 0.72 kg CO_2 + 0.77 kg H_2O

Theoretically 80 % of N in MEA is released as ammonia. In water at neutral pH ammonia reacts with water to form ammonium:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

Thus, microbial oxidation of MEA will lead to a substantial pH increase. To prevent this pH increase 0.63 kg H_2SO_4 has to be added per kg MEA metabolized.

3.3 Biodegradation of aminomethylpropanol (AMP)

Studies of the microbial degradation of AMP do not seem to have been reported in the literature. However, according to Hanna Instruments (2008), it is classified as “biologically not readily degradable” (*i.e.* 40 % biodegraded in 28 days using the OECD 301 D test (closed bottle)). The pass level for readily biodegradable is 60 % in 28 days.

If we assume that 50 % of the carbon in AMP goes to biomass and 50 % to CO_2, a theoretical mass balance is:

$$\tfrac{1}{2}\ (CH_3)_2C(NH_2)CH_2OH + 1.7\ O_2 \rightarrow CH_{1.8}O_{0.5}N_{0.2} + CO_2 + 1.4\ H_2O + 0.3\ NH_3$$

or: 1.00 kg AMP + 1.22 kg O_2 → 0.55 kg cell mass (d.w.) + 0.11 kg NH_3 + 0.99 kg CO_2 + 0.57 kg H_2O

Theoretically 60 % of N in AMP is released as ammonia, and microbial oxidation of AMP will therefore increase pH. To prevent this 0.32 kg H_2SO_4 has to be added per kg AMP metabolized.

3.4 Oxidation of ammonia (NH_3)

Under aerobic conditions ammonia is oxidized to nitrate (NO_3^-). This process is called nitrification, and the bacteria responsible for the process use CO_2 as carbon source and derive their energy from the oxidation of NH_4^+ to NO_3^-. Based on Ødegaard (1992) the mass balance is:

$$NH_4^+ + 1.865\ O_2 + 0.1\ HCO_3^- \rightarrow 0.1\ CH_{1.8}O_{0.5}N_{0.2}\ \text{(biomass)} + 0.98\ NO_3^- + 1.03\ H_2O + 1.88\ H^+$$

$$\text{or: } 1.00\ \text{kg}\ NH_4^+ + 3.32\ \text{kg}\ O_2 + 0.34\ \text{kg}\ HCO_3^- \rightarrow 0.14\ \text{kg biomass} + 3.38\ \text{kg}\ NO_3^- + 1.03\ \text{kg}\ H_2O$$

The bacteria responsible for the nitrification process are slow-growing and therefore require a long residence time in the bioreactor. They loose out in the competition with heterotrophic bacteria and the concentration of organic material in the bioreactor must be low. However, it is possible to establish conditions where degradation of organic material and nitrification takes place simultaneously. It should be noted that nitrification produces acid and may thus counteract the pH increase due to formation of ammonia.

If ammonium is released to the aquatic or marine environment, the nitrification process will occur there. The high oxygen requirement for the process may then become a problem, in addition to the fertilizer effect that particularly in marine environment may lead to extensive growth of algae[1]. A number of technical solutions to promote bacterial nitrification followed by bacterial denitrification (formation of N_2 from NO_3^-) have been developed in wastewater treatment (see for instance Ødegaard, 1992), and may be one option for the treatment of the ammonia rich wastewater from the waste gas purification unit.

3.5 Biodegradation of nitrosamines

Microbial degradation of nitrosamines appears to be by co-metabolism (*i.e.* it is degraded together with another substrate) (Krauss *et al.*, 2009). No microorganisms have been isolated so far that could utilize nitrosamines as sole substrates for growth (Krauss *et al.*, 2009). In wastewater treatment plants the removal efficiency is generally good (>60 %) when nitrosamines are present in concentrations above 10-15 ng/L. Below this threshold, the degradation is poor, possibly because of substrate competition (Krauss *et al.*, 2009). Current internationally accepted limits for notification are in the order of 10 ng/L. This simply means that where NMDA (and a few other nitrosamines) are detected above this level the water authorities should inform regulatory bodies who would typically decide whether or not action is needed (Mlongo *et al.*, 2009).

3.6 Other additions

The amines in the waste gas will provide the necessary carbon and nitrogen for growth. However, microorganisms also require other nutrients and growth factors in order to function and produce new cells. These include phosphorous, sulfur, vitamins, and trace elements. If pH is controlled with sulfuric acid, the two main minerals that have to be added are P (as PO_4) and K. A rough estimate is that bacteria contain 1.5 % of dry weight (d.w.) potassium and 3 % phosphorous. Added as KH_2PO_4, this corresponds to 0.05 kg per kg MEA metabolized and 0.07 kg per kg AMP metabolized. However, a well functioning biological purification process includes protozoa and other organisms that eat bacteria and fungi and thus re-circulate some the mineral nutrients.

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[1] In marine environments nitrogen is often the growth limiting nutrient, in fresh water the growth limiting nutrient is often phosphorous)

4 PRINCIPLES OF BIOLOGICAL WASTE GAS TREATMENT

4.1 Operation principles

Biological waste gas purification technology currently includes bioreactors known as: *biofilters*, *biotrickling filters*, *bioscrubbers*, and *membrane bioreactors*. The mode of operation for all these reactors is very similar. Gas containing volatile compounds is passed through the bioreactor where the volatile compounds are transferred from the gas phase into the liquid phase. Microorganisms, such as bacteria or fungi, growing in the liquid phase, usually as a thin slimy layer called a biofilm on the carrier material, degrade the compounds dissolved in the liquid phase. The microorganisms responsible for the biodegradation normally grow as a mixture of different microorganisms. Such a mixture of different bacteria, fungi, and protozoa depends on a number of interactions and is often referred to as a microbial community. Often the waste gas contains many different chemical compounds. The remarkable aspect of the microbial community is that it generally develops to a composition so that all these different chemicals are removed and metabolized simultaneously.

4.2 Biofilter

In a biofilter the gas is passed through a bed packed with organic carrier materials, e.g. compost, soil, or wooden bark, where the microorganisms grow as a biofilm on the filter material (Figure 1). The nutrients necessary for growth are supplied by the organic matter. An important control parameter is the moisture content of the overall carrier matrix, which must be between 40 and 60 % (w/w). To avoid dehydration, the air is generally humidified before entering the biofilter. In addition water is often sprayed intermittently over the biofilter to maintain the required humidity.

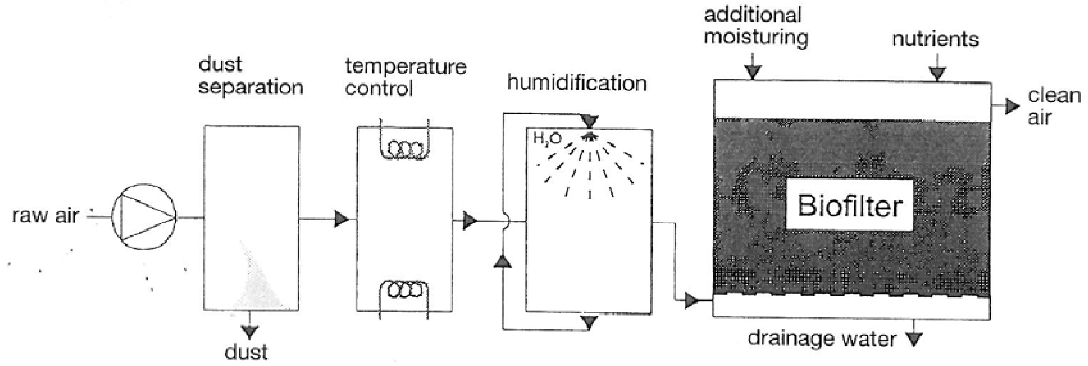

Figure 1 *Outline of a biological filter system (Fischer, 2000)*

In order to prevent a substantial pressure loss as the gas passes through the filter, the thickness of the biofilter is usually limited to 0.5-1 m, and biofilters therefore often have a large “footprint”. Normal filter volume loads are 50-100 m^3 gas per m^3 filter and hour (Fischer, 2000). Thus, for a gas load of 1 million m^3 per hour a filter area of 10 to 40 thousand square meters is required. For calculation purposes a filter area of 20 000 m^2 and a filter volume of 15 000 m^3 is assumed.

According to Fischer (2000) the specific investment costs for a large single-level biofilter (approx. 1000 m^2) are approx. 300 EUR per m^2. For a filter that can treat 1 million m^3 per hour this means 6 million EUR, but it seems reasonable to assume that the cost per m^2 for a 20 thousand m^2 filter will be lower than for a 1000 m^2 filter. The operating costs of a biological filter system consist of costs for energy, personnel, maintenance, and filter materials (Table 1).

Table 1 *Operating costs for a biofilter according to Fischer (2000) and estimated costs for a very large biofilter capable of treating 1 mill. m^3 gas per hour*

Cost	**Cost for a 1000 m^2 filter**	**Estimated costs for a 20 000 m^2 / 15 000 m^3 filter**
Energy (with compost as filter material)	1.8-2.5 kW per 1000 m^3	27-38 kW
Personnel requirement	0.8-1.0 hour per m^2 filter area	16 000 – 20 000 man-hours
Maintenance	8-9 % of investment costs	400 000 EUR per year
Filter material (life-time 2-4 years)	20-50 EUR/m^3 + considerable transport costs of up to 100 % of the pure costs of materials depending on the distance and the bulk density.	>300 000 – 750 000 EUR
Material disposal	Depends upon waste gas composition and filter material. It may be suitable as fertilizer (compost) or, in worst case, a toxic waste.	
Water consumption	1.0-1.5 m^3 water per m^2 filter area and year.	20 000 – 30 000 m^3 per year

4.3 Biotrickling filter

In a biotrickling filter (Figure 2) the pollutants are transferred from the gas phase via a thin water film to the microorganisms that grow as a biofilm on a packing material. However, the packing materials are made of chemical inert materials such as plastic rings. Because nutrients are not available in these materials, they have to be supplied to the microorganisms by re-circulating a liquid phase through the reactor in co- or counter current flow.

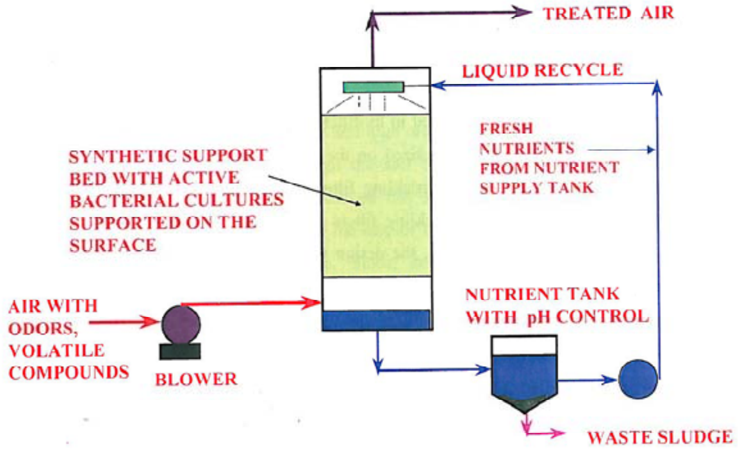

Figure 2 *Schematic outline of a single-stage counter-current biotrickling filter (Govind, 2009).*

Govind (s.a.) gives capital and operating costs for a biotrickling filter used for iso-pentane treatment with an inlet concentration of 1000 ppm and a destruction efficiency of 95 % as a function of the waste gas flow (8 000 - 25 000 m^3/hour). If we extrapolate these cost figures to a gas flow rate of 1 million m^3 per hour, the capital cost is approx. 2 million USD and the operating cost approx. 1 million USD per year.

A possible problem with biotrickling filters is plugging and channeling due to extensive microbial growth on the support material.

4.4 Bioscrubber

A bioscrubber (Figure 3) consists of two units, an absorption tower where pollutants are absorbed in a liquid phase, and a bioreactor where microorganisms growing in suspended flocs in the water degrade the pollutants. The effluent of this unit is re-circulated over the absorption tower in a co- or counter current way to the flow of the waste gas. Bioscrubbers will after a short period of operation of develop a biofilm on the fixed internal parts of the absorption column. This can lead to partial blocking and channeling if the space for flow is too small, as is usually the case in packed columns. The use of internal parts with an open structure and trickling densities high enough (>20 $m^3/m^2 \cdot h$) that the shear force prevents a large biomass accumulation on the internal parts are possible countermeasures to ensure that gas and liquid can freely pass the scrubber.

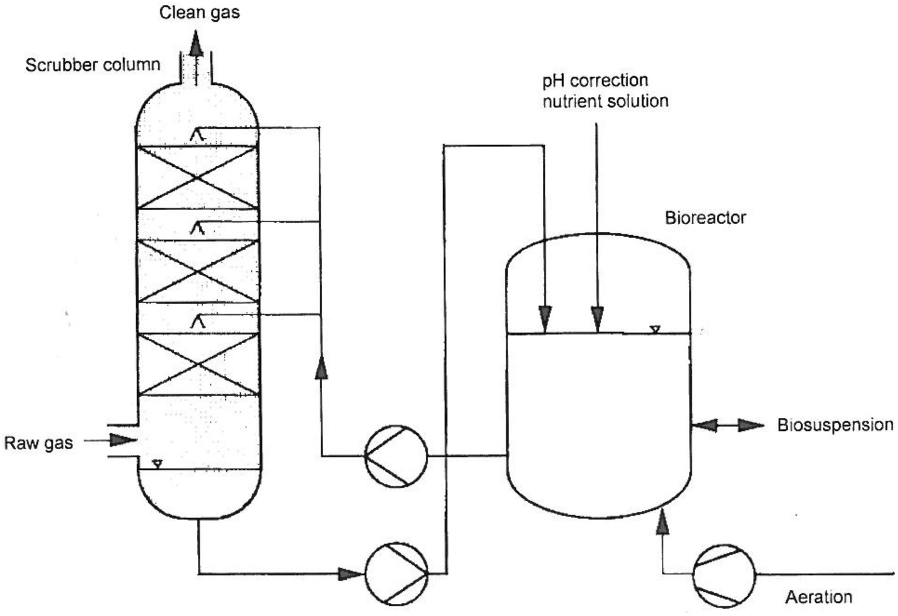

Figure 3 *Flow diagram of a bioscrubber for waste air cleaning (Schippert & Chmiel, 2000).*

Bioscrubbers are particularly suitable for waste gas cleaning if a biological wastewater treatment plant already exists and if the components from the waste gas stream cab be easily dissolved in water and are biologically degradable.

4.5 Membrane bioreactors

In a membrane bioreactor the waste gas stream is separated from the biofilm by a membrane that is selectively permeable to the pollutants (Figure 4). One side is in contact with a liquid phase supplemented with nutrients while the other side is in contact with the waste gas stream. The advantage is that there is no direct contact between the microorganisms and the gas phase and clogging due to microbial growth is therefore not a problem. Furthermore, humidification of the crude gas is not necessary and long term operation with mono-cultures is possible. However, so far no large scale biofiltration units based on membrane reactors have been constructed (Reiser, 2000; Kumar et al., 2008).

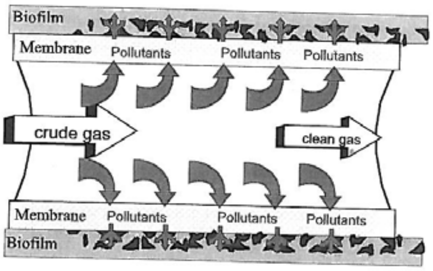

Figure 4 *Schematic picture of the mass transfer using dense membranes in biological waste gas purification (Reiser, 2000)*

5 INDUSTRIAL SCALE BIOLOGICAL WASTE GAS TREATMENT

There are many hundred biological waste gas treatment units in operation worldwide today (Chitwood & Devinny, 2000). Various biofilter designs appear to most common, but also biotrickling filters and bioscrubbers are frequently employed. Most full scale biological waste gas treatment units are designed to remove H_2S, CS_2, and various volatile organic compounds such as phenol, styrene, toluene, formaldehyde, organic acids, alcohols and dichlorethane. Units handling gas flows of up to 90 000 m^3/hour (biofilter) (Chitwood & Devinny, 2000), 160 000 m^3/hour (biotrickling filter) (Kraakman, 2005) and 62 500 m^3/hour (bioscrubber) (Kraakman, 2005) have been reported. Removal of ammonia and other odorous compounds from livestock facilities with biofilters appear to be fairly common, but units handling industrial waste gas containing ammonia and/or amines appear to be less frequently used. However, biotrickling filters have been used to treat 1000 m^3/hour waste gas containing phenol, formaldehyde and ammonia from a resin-laden factory (Arnold *et al.*, 1997) and 12 000 m^3/hour waste gas containing phenol and ammonia from a rock wool manufacturer (Rydin *et al*., 1994), and a bioscrubber was used to treat 41 000 m^3/hour waste gas containing ammonia and odorous compounds from a cigarette production facility (Frohlich, 1994).

6 CONCLUDING REMARKS

Biological waste gas treatment is a possible secondary treatment after water scrubbing of the waste gas from the amine-based CO_2 capture unit. However, the amount of gas to be treated is roughly an order of magnitude larger than what is treated in the largest existing plants today. It is not possible at this stage to make a final selection between the three basic techniques; biofilter, biotrickling filter, and bioscrubber, but at first glance a bioscrubber appear to be the most interesting solution due to the high solubility of most of the pollutants. An alternative to a bioscrubber could be a second water scrubber. Because the design of the bioscrubber must take into account the formation of biofilm, the absorption process will probably be a less efficient than in a water scrubber. On the other hand, a bioscrubber may use an activated sludge wastewater treatment unit (see below) as the bioreactor (see Figure 3) and will then not increase the volume of wastewater to be handled. Further studies are required to reach a final conclusion, but since most of the pollutants from the amine-based CO_2 capture unit are highly water soluble and has alkaline properties, a water/acid wash may be better option than a bioscrubber. The subsequent treatment of the generated wastewater to remove the dissolved compounds should, however, be biological.

The wastewater from water scrubbers will contain a mixture of amines, degradation products of amines and ammonium. This water cannot be discharged to the environment without treatment, and an aerobic activated sludge wastewater treatment unit is likely to be part of the system. Here the amines and their degradation products will be metabolized by microorganisms to CO_2 + H_2O + NH_4^+ + biomass, and part of the ammonium probably further oxidized to nitrate. The oxygen transfer rate in conventional activated sludge reactors is typically 0.1-0.3 kg $O_2/m^3 \cdot$ hour (3 to 10 mmol $O_2/L \cdot$ hour), but may be up to 2.5 kg $O_2/m^3 \cdot$ hour in more advanced high intensive processes (Aker Kværner, 2005). A load of 250 kg AMP per hour requires 305 kg O_2 per hour for oxidation. If we assume some oxidation of ammonium to nitrate a total requirement of around 500 kg O_2 per hour appears likely, and an activated sludge reactor (conventional design) with a volume of 3000-5000 m^3 should be sufficient.

The biomass in the effluent from the activated sludge unit is easily be removed by settling and the concentration of dissolved organic material should be fairly low, but the effluent will have a high content of dissolved ammonium and nitrate. A rough estimate indicates a yearly discharge of 3500-4000 ton N as ammonium and nitrate. For comparison, 104 000 ton N as inorganic fertilizer was used in Norway in 2003 (Store Norske leksikon, 2010). It is not likely that the regulatory authorities will accept that this water is discharged without further treatment. One solution is biological nitrification followed by biological denitrification to nitrogen gas. This is standard wastewater treatment technology today and used in the treatment of municipal wastewater many places. However, a reuse of the nitrogen compounds in the effluent as fertilizer, preferably in agriculture, would be a more environmentally acceptable, and may potentially be more economic than transformation to nitrogen gas. Further elaboration of this is, however, outside the scope of this report.

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