GASEOUS EMISSIONS FROM AMINE BASED POST COMBUSTION CO_2 CAPTURE PROCESSES AND THEIR DEEP REMOVAL

Report: 2012/07

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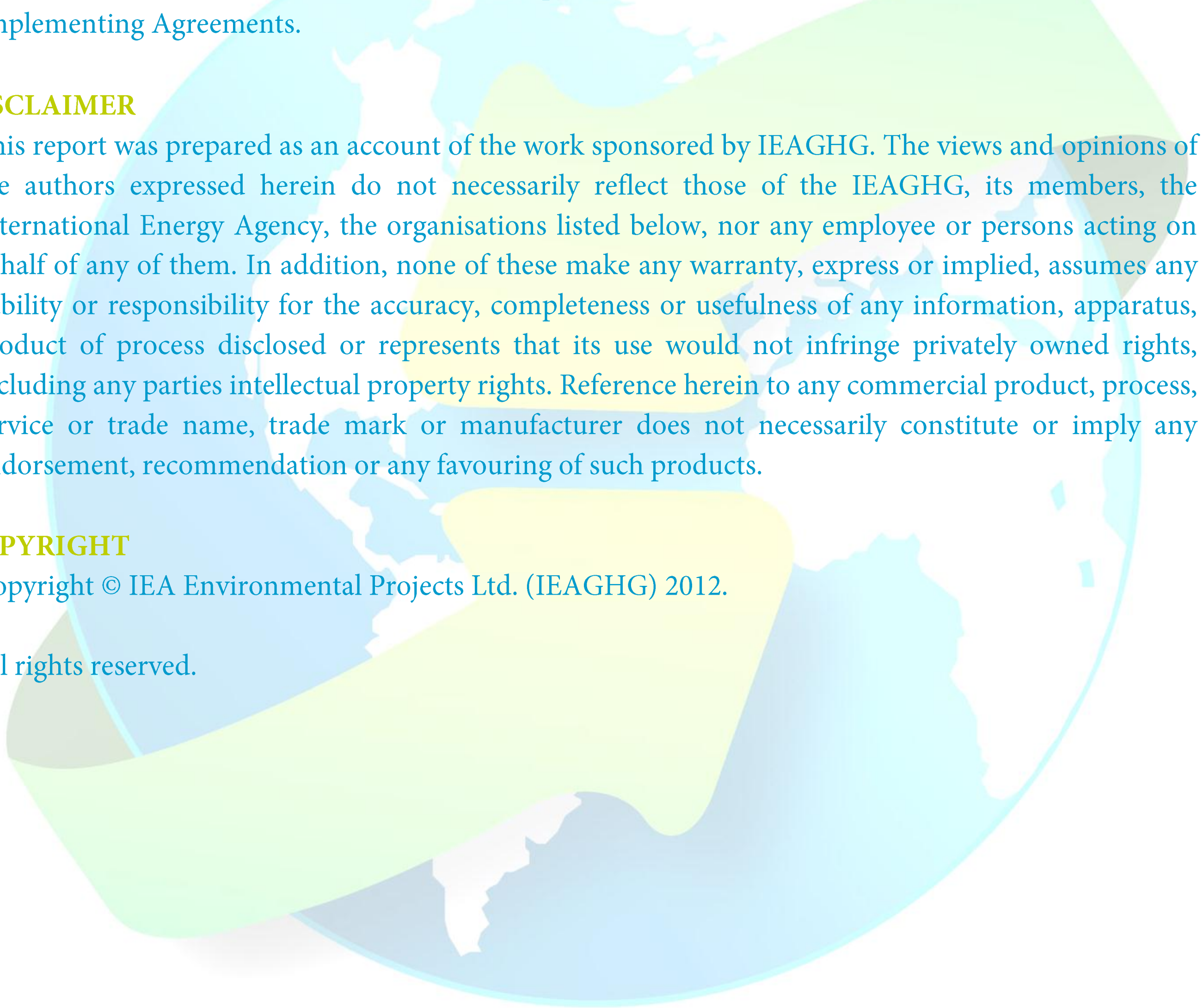

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GASEOUS EMISSIONS FROM AMINE BASED POST-COMBUSTION CO_2 CAPTURE PROCESSES AND METHODS FOR THEIR DEEP REMOVAL

Introduction

Amine based post combustion CO_2 capture technology is widely seen as a promising option for reducing atmospheric emissions of CO_2. Great efforts have been made to develop and demonstrate this technology. However less attention has been given to the likely emissions of amines and their degradation products, some of which are well known to be harmful to human health and the environment. The components of concern do not currently figure in the emission slate of power plants. Standards and legislation are thus not fully developed for their control, particularly considering the scale on which CCS plants may be deployed. A full understanding of the nature of the likely emissions and the limits which need to be imposed is necessary so that appropriate improvements in the capture process can be made to protect human health and the environment from adverse impacts. This study was executed to identify the chemical species likely to be emitted, estimate the levels of emission expected from the present generation of capture plant designs, assess what emission limits might be applied and research the process modifications needed to meet these limits.

Approach

The study was awarded to CSIRO, Australia on the basis of competitive tender. The first step was to make estimates of the most likely chemical emissions. In this report this was done on the basis of emissions from amine based inhibitor-free solvents, particularly those based on MEA, ammonia and amino acid salts, and their degradation products. MEA was chosen for more detailed assessment as this is currently the major constituent of most absorption solvents used in post combustion capture systems. Chemical emissions and wastes from the CO_2 capture process fall into three categories.

(1) Physical entrainment and evaporative loss of amine and its degradation products into the gas streams
(2) Discharge of organic degradation products, heavy metals and heat stable salts in the liquid waste streams
(3) Fugitive emissions during plant operation and handling of chemicals

This report only focuses on the first of the above mentioned emissions.

Estimates of gaseous emissions were made in two ways. First values mentioned in extensive literature on the amine based capture processes were examined enabling some idea of the likely range of emissions to be assessed. Second a simulation of the complex degradation reactions and the processes which occur in CO_2 capture plant has been made in order to provide an alternative assessment. Sampling and analysis of traces of chemicals in flue gas is difficult and most laboratory, pilot and technical rather than environmental performance of the process. As a result there is both wide variation and uncertainty in the estimates for gaseous emissions.

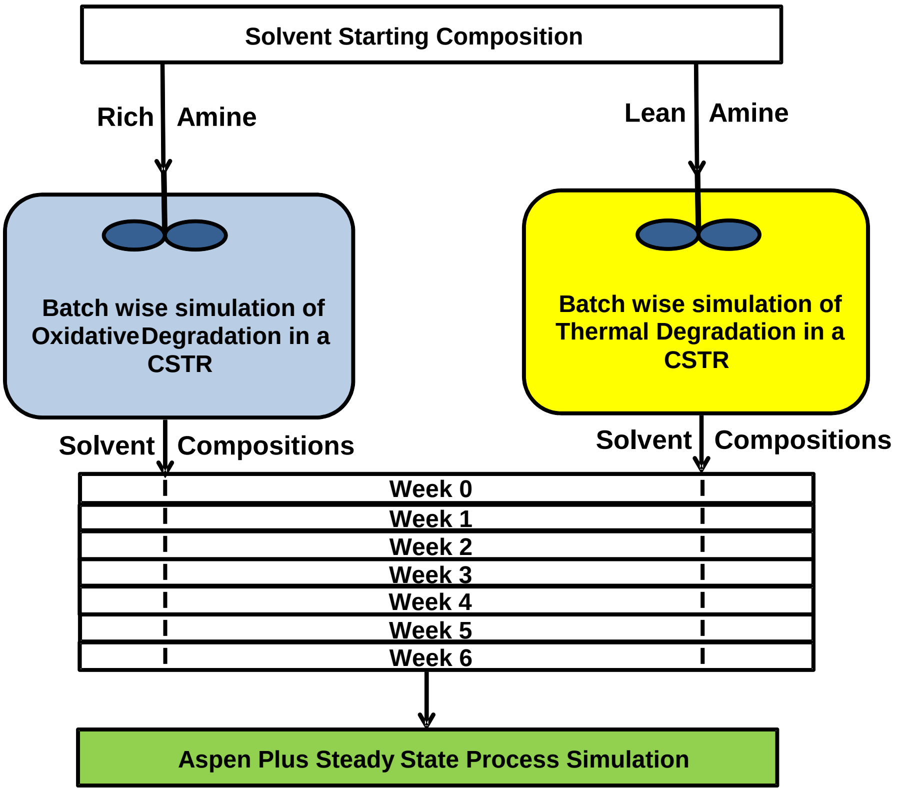
Baseline PCC processes

Two processes based on the use of MEA solvent without addition of other additives were chosen as base cases for evaluation of chemical emissions via simulation. These processes were coal fired ultra-supercritical steam plant and gas fired combined cycle plant as defined in studies carried out previously for IEAGHG. These processes use a single stage water wash after the CO_2 absorber and for simulations cooling was applied so that flue gas exit temperature was reduced to 45°C. This choice is important because the levels of volatile compounds are greatly affected by temperatures in and after the absorber. Degradation of MEA proceeds via two main pathways, thermal degradation and oxidative degradation both of which have been considered in this study.

Modelling of Amine degradation and related emissions

Modelling of the amine degradation process was done using ASPEN plus and was divided into two elements. First was to build a steady state simulation of the capture process and second was to model the progress of the known chemical degradation reactions with time. It is not possible to use the steady state simulator for the time dependent reactions. Instead these were simulated in two separate stirred tank reactors one for the thermal and another for the oxidative degradation reactions.

Depiction of MEA Degradation Calculation Routine



As the MEA solvent in an absorption plant degrades some degradation products will build up, for example heat stable salts, and these are removed from a slip stream of solvent either continuously or batch wise in a reclaimer. The reclaimer recovers amine and concentrates the degradation products for disposal as waste. If the batch-wise operation is chosen the composition of the solvent gradually changes until the reclaimer is re-started. This is generally every few weeks. The simulation was based on batch-wise reclamation as follows. The stirred tank reactors were allowed to run for up to 6 weeks and compositions of solvent were derived at the end of each week. These compositions were then used in the steady state simulator to calculate gaseous emissions from the absorber at that point in time.

Simulation runs were made in which it was assumed that no droplet carryover was occurring and also with carry over set at the worst prediction for demister performance found in the GPSA handbook namely $0.13M^3$/million m^3. This is a very high value but it enables a worst case scenario and the split between vapour and liquid carryover effects for each component to be estimated.

The reactions modelled were based on the open literature. However not all reactions could be modelled and not all components were available in the ASPEN database. Where this was a limitation the reactions either had to be omitted or in the case of a missing component data a component with similar volatility was chosen for the steady state simulator. There were also some reactions, one notably involving DEA, where there are differences of opinion as to what reactions are occurring.

Literature data on emissions

This report contains extensive data and references both on measured and estimated emissions but also on the reactions involved in amine degradation. The chemical pathways, equilibrium and kinetic data chosen for modelling the degradation reactions are presented. In addition the estimated and measured emissions from a number of laboratory investigations and demonstration plants are reported.

Estimated emission levels from simulation

The results from simulation are different but not in conflict with those which have been measured in practice. Even though very pessimistic assumptions have been made about droplet carry over there are some measurements which are higher than simulator predictions. On the other hand the effect of droplet carry over is often not dominating particularly for the more volatile components. This report summarises the expected ranges for both the USC coal and NGCC cases in a table of maximum and minimum expected values for all compounds expected to be detectable. The maximum values calculated in the simulations are shown below.

There were considerably higher values for emissions found for the gas fired case but this was largely because the process conditions and line up of the water wash were based on a relatively early study done for IEAGHG. This illustrates the importance of designing for the optimum temperature conditions in the absorber and water wash sections of post combustion capture processes in order to minimise emissions from the solvent and its degradation products.

<table>
<tr><th colspan="2">Maximum emission levels from simulations of coal and gas fired MEA based CO_2 post combustion capture plant</th></tr>
<tr><th>Component</th><th>mg/Nm^3 dry CO_2 lean Flue gas</th></tr>
<tr><td>MEA</td><td>5.5</td></tr>
<tr><td>NH_3</td><td>1.14</td></tr>
<tr><td>DEA</td><td>0.254</td></tr>
<tr><td>FORMALDEHYDE</td><td>0.314</td></tr>
<tr><td>ACETALDEHYDE</td><td>0.326</td></tr>
<tr><td>ACETONE</td><td>0.422</td></tr>
<tr><td>METHYLAMINE</td><td>0.26</td></tr>
<tr><td>ACETAMIDE</td><td>0.0002</td></tr>
</table>

Three principle heavier degradation products Oxazolidone, 1-(2 Hydroxyethyl) imidazolidone-2 (often abbreviated to HEIA) and N-(2-Hydroxyethyl)-ethylenediamine (often abbreviated to HEEDA) which have slight volatility were found to have extremely low emission levels in the simulation. The single stage water wash is very effective in removing heavier components.

Emission levels from literature

This report includes data from a number of references which show that emission levels which have been measured have been both substantially higher and lower than the simulated values. In some cases the exact process conditions are not available The best general conclusion that can be drawn is that there is potential for chemical emissions although with a one stage water wash at close to ambient temperature these emissions can be lowered but not reduced to the point that they can be considered as negligible.

Of particular interest are references in the literature on the formation of nitrosamines. The formation of these components was not included in the simulation as the exact mechanisms are not known yet. Nitrosamines have been detected in the solvent by some researchers but the exact mechanism of their formation is not agreed. Nitrosamines are known to be a class of compound which can be highly carcinogenic. Their formation is thought to be due to reactions of NOx with secondary/tertiary amines but MEA itself is not thought to be the precursor in stable nitrosamine formation. The nitrosamines detected are N-nitrosodiethanolamine (NDELA) and nitrosodimethylamine (NDMA). Diethylamine (DEA) was also detected in the solvent and may be a precursor for these nitrosamines although the origin of the DEA is uncertain. A small amount of the nitrosamine (NDELA) has been measured in the Trona plant in California at the level of nearly 3 μmol/ml but this level may however only have been reached after a long build up period. To estimate whether this would result in an emission the simulation was run with this high amount added to the solvent. However this component is not in the library of ASPEN so the lighter dimethyl nitrosamine was substituted to check whether any emission was possible.

The results of the simulation of this extreme case predicted between 2 and 6 mg/Nm^3 of this component in the exhaust flue gas mainly due to its high vapour pressure and not due to liquid carry-over. Thus with a single water wash there is a remote possibility for detectable levels of nitrosamines to be emitted especially if they are allowed to build up in the solvent over a very long period of time. Further work needs to be done to demonstrate conclusively that they will not be emitted.

Processes to reduce chemical emissions

The processes currently applied for reducing gases and fine droplets are cooling, demisting and water washing. The reason that a single stage water wash is not effective is that the water has to be circulated and the chemicals which are washed out build up. They then exert a vapour pressure and the water with contaminants can be entrained as droplets. The simulations show clearly the value of cooling the outlet stream as far as possible and one good way to do this is to apply intercoolers in the absorber column so that the top temperature is kept low.

Increasing the number of scrubbing stages is an option but references suggest that while this further reduces the emissions levels it is only partially effective. Washing with an acid solution on the other hand appears from literature sources to be rather effective and this is because most of the contaminants react with acid. A range of choices for the acid are available through strong inorganic acids, weak organic acids even to carbonic acid itself. The weaker acids might allow captured MEA to be regenerated.

Other more exotic measures were investigated including exposure to UV radiation, adsorption on solid beds and, cryogenic cooling. UV radiation appears to be an option for dealing with Nitrosamines as it causes their decomposition. Solid adsorption beds would need to be regenerated by vacuum rather than pressurised operation or temperature swing because parasitic energy losses would otherwise be unacceptable.

A major difficulty would be selecting an active adsorbent which will not be unduly affected by the water vapour in the effluent flue-gas. It would certainly not be practical to dry the entire flue gas stream. Limited cryogenic cooling could improve emissions marginally as lowering temperature is already known to improve the effectiveness of water scrubbing. However it is costly since the whole stream must be cooled although some energy could be recovered in a regenerative heat exchanger. Cooling could not go below the freezing point and, unless reheated, the flue gases would no longer be buoyant.

This report examines the performance of various types of demister available on the market. Demisting is particularly important for complete removal of MEA as this is the component which will have the highest concentration in the wash system liquids. Three mechanisms are employed in the devices used for demisting. Impingement devices in which droplets collide with surfaces on which they subsequently coalesce and drain away. Inertial devices where gas flows through tortuous pathways which liquid droplets cannot follow because of their inertia and devices based on Brownian motion where very fine droplets impinge on a surface due to their irregular Brownian motion. These devices are described in some detail in this report which shows several examples of how separation efficiency correlates with droplet size. The most appropriate demisting device is identified as being the Swirl Mist Eliminator (SME). This combines high efficiency, good liquid drainage properties (important during overloading or process upsets) and space requirements which allow for it to fit inside the diameter of absorber and wash columns. Although they have no moving parts, they are more complex and likely to be more expensive than wire mesh and corrugated vane type demisters.

Emission standards and legislation

This report contains a comprehensive overview of the various directives, regulating bodies and emission standards which apply. This reveals that in general emission levels for the new chemical substances which might be emitted from CO_2 post combustion capture have yet to be established. Environmental and health data from industrial uses might help in this process but is in itself not a sufficient basis for defining emissions levels. In the case of compounds which are known or suspected carcinogens regulation is most likely to be to adopt Best Available Techniques (BAT) rather than to set an emission standard. Often no numerical standard is set for carcinogens as it is not possible to define a lower safe limit.

The industry may come up against three main types of emissions limitation. The first is simply the acceptable concentration in the air to safeguard human health. The second is the imposition of upper limits for the total annual emission industry of a substance in a country or region. For example ammonia is regulated in this way in Europe. This report however shows that the potential emissions from post combustion capture amine based plants of all major sources of CO_2 were captured would only contribute around 5% of this allowance. The third is limitations due to cumulative and instantaneous effects on plants and their habitats. For example nitrogen and sulphur emissions may be limited to avoid eutrophication and acidification.

Given that the acid wash process appears to be rather effective and that high efficiency demisting devices are available a conclusion could be made that these or similar enhanced measures will become the de facto standard when large scale CO_2 capture plants are deployed. Also the addition of a UV process to ensure complete elimination of nitrosamines is kept in reserve in the unlikely event that the acid washing and high efficiency demisting processes are found to be insufficient.

New solvent systems and their emissions

The likely emissions from two alternative systems for CO_2 absorption were examined. Amino acid salt solutions have relatively fast rate of CO_2 absorption, higher CO_2 selectivity, high stability towards oxygen, very low vapour pressure, high biodegradability and favourable binding energy but lower CO_2 absorption capacity than MEA solution. Due to these favourable properties, the amino acid salts have been deployed for commercial scale acid gas removal processes in the past, such as the Alkazid process. Recently, with the increase in interest in CO_2 post combustion capture, Siemens has developed a new process for CO_2 capture from power stations.

As reported in the literature, this process produces an insignificant amount of degradation products and has lower emissions to atmosphere.

Aqueous ammonia processes have also been claimed, in the literature, as an effective separation with potentially low emissions despite the fact that ammonia is toxic and corrosive. The main attractions are claimed to be ammonia's estimated 3 times more CO_2 uptake capacity, relatively higher stability, no interference from SO_x and NO_x on the ammonia capture efficiency and less corrosive nature as compared to MEA. It is also reported in the literature that the chemical regeneration energy required by ammonia is about three times less and this is reflected in reduction in capital and operating cost by about 15% and 20% as compared with MEA. Researchers are currently trying to reduce ammonia losses and emissions. It is important that the performance of ammonia process is thoroughly evaluated to ascertain the operating costs, energy consumption and emissions prior to any construction of commercial scale plant is considered.

Both amino acid salt and aqueous ammonia processes seem to have an insignificant extent of solvent degradation and the base case emissions of ammonia is reported to be below 1 and 10 ppmw, respectively. There is no report on the list of any other degradation products (than ammonia) formed in these processes. On application of acid wash the emissions from these processes could be brought down to near-zero. UV methods are probably not required for these processes as there is no report on nitrosamine emissions from them. However the acid treatment process, recirculation or disposal of acid and salt, have to be further studied in the laboratory prior to implementation at larger scale.

Expert reviewer's comments

Some reviewers were concerned that the choice of MEA as the basis for this study was restrictive and that the potential of other solvents was not covered and even masked. The selection of a very high worst case liquid carry over figure was considered by some to be inappropriate and leading to suggestions that emissions might be higher than is realistic. Both these comments are acknowledged as valid. On the first the simulation of alternative solvents was considered beyond the scope of the study resources. On the second point the high value for worst case carry over was retained but the text modified to make clear that this represents an unlikely worst case scenario.

Some reviewers felt that the way nitrosamine levels in processes and literature was reported over-accentuated the possible risk of such emissions and the reality that they are very unlikely to be present at detectable levels. The text was modified to reflect this concern although the basic figures are still reported.

Based on reviewer's comments the tone of the report was altered to reflect that the extent of knowledge in this area is incomplete and is still undergoing rapid development. A considerable number of specific comments were received and the authors were very grateful for this extensive contribution and have amended many details in the report as a result.

Conclusions

The main conclusions of the report can be summarised as follows:-

- Detectable levels of lighter components will probably be emitted to atmosphere from amine based capture plants employing single water wash technology.
- Emissions to air of heavier degradation products will be at well below detectable levels.
- Application of an additional acid wash is an effective way of eliminating emissions of the lighter components.
- The preferred choice of demister seems to be the Swirl Mist Eliminator (SME).
- Emissions standards are not yet set for many of the substances which are likely to be emitted.
- Stringent emissions standards and regulatory requirements to adopt best available techniques can be expected particularly so if even the presence of trace amounts of known carcinogens are confirmed.
- More research into emissions and their measurement is required.
- Regulatory authorities have much work to do to create an appropriate emission standards which can be applied to MEA based CO_2 capture processes.
- Some alternative solvents have lower emissions but may still need to apply similar additional clean up steps

Recommendations

Further work on chemical emissions from solvents should be promoted and in particular pilot and demonstration projects should be encouraged to monitor actual measurements of these emissions during normal operation and make detailed measurements during test runs. They should also be encouraged to measure and report on the build-up of the full range of degradation products with time. Requests for this type of information should be included in surveys of demonstration projects under the Phase 2 of the “What We have Learned” data collection and analysis initiative.

Work is also needed to assess the fate of any emissions in the atmosphere and the programme could consider carrying out a study of available results once a substantial body of scientific information on this is available.

The inclusion of an acid wash in the post combustion capture process appears to offer a simple but robust catch all solution to this emerging issue. Further work needs to be done to establish how this should be implemented including whether a final water wash is needed. Development of this could be the domain of process licensors but this could be controversial given the additional cost and complexity implications. The programme should in the first instance promote adoption of a completely “clean” solution but could also consider commissioning an engineering contractor to further study and cost out suitable designs.

Gaseous Emissions from Amine Based Post-Combustion CO_2 Capture Processes and Various Methods for their Deep Removal

(IEA/CON/10/183)

Report Prepared by
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CONTENTS

EXECUTIVE SUMMARY

In the last decade a number of technologies has been developed, evaluated and demonstrated for capturing carbon dioxide produced at the power stations burning fossil fuels. Monoethanolamine (MEA) based CO_2 capture technology, is widely seen as one of the promising options for reducing atmospheric emissions of CO_2, particularly from carbon intensive processes such as natural gas and coal based power plants. While great efforts have been invested to demonstrate this technology as a feasible option available to the power industry, little attention has been given to the likely emissions of amine and its degradation products, some of which are well known to be harmful to human health and the environment. At present, the anticipated emissions may present a serious concern and require a rigorous scientific evaluation prior to mass implementation of CO_2 capture technology so that appropriate improvements in the process can be made to protect human health and the environment from any adverse impacts.

It is expected that all amine-based CO_2 capture plants will emit some compounds that are generally different to those typically associated with natural gas and/or coal combustion. Emissions of these new compounds to the environment are likely to be via three major pathways: (1) physical entrainment and evaporative loss of amine and its degradation products into the gas streams, (2) discharge of degradation products, heavy metals and heat stable salts in the liquid waste streams, and (3) fugitive emissions during plant operation and handling of chemicals.

This report evaluates the emission from the PCC technology that uses amine based inhibitor-free solvents, particularly MEA, ammonia and amino acid salt based solvents. It identifies shortcomings in terms of the environmental performance of existing PCC technology. It also evaluates various emission control methods that may be applied to minimise the emissions particularly from MEA and other amine technologies. All these aspects of the study are covered in the four sections of this report. A complete evaluation of environmental impact of the amine based process would involve assessment of all direct discharge of waste material from the process and the fates of these compounds, including chemical transformations that occur after their discharge. However, it is to be noted that only gaseous emissions are evaluated in this report and liquid and solid emissions are considered as beyond the scope of this study.

Emissions from PCC process

This section summarises the modelling results of emissions from an aqueous MEA-based post combustion CO_2 capture (PCC) process that was coupled with flue gas either from a coal fired ultra supercritical (CFUS) or a natural gas fired combined cycle (NGCC) power plants. The process flow sheet and operating conditions were derived from an earlier IEA-GHG study report[1]. In this study the MEA is considered as representative of amine based solvents for the reason that MEA appears to be the basis for many technology developers at present and for its known performance with natural gas sweetening processes. It should be noted that although the extent of degradation of solvent will depend on operating conditions and the type of amine used, the strategies and methods to minimise the emissions related to solvents comprising other amines may not be drastically different. With appropriate optimisation and modifications, these emission control methods and strategies could be applied to any of the amine based post combustion carbon capture processes.

During the current study the following aspects were considered:

- Thermal and oxidative degradation of MEA is recognised as the major reason for the formation of degradation products with different potentials to escape the plant to the atmosphere. To estimate thermal degradation of MEA, the reaction mechanism and kinetic model described by Davis[8] has been used in the simulation. The model described by Uyanga[7] was used to estimate oxidative degradation of MEA.
- Since ASPEN process simulation was developed for estimating mass and energy balance for steady state process, it was not possible to estimate dynamic rise in MEA degradation products. It was therefore decided to estimate equilibrium concentrations of degradation products reached between two consecutive reclamations of the solvent. The solvent reclamation, usually takes place every 3rd or 4th week when degraded solvent is removed via a reclaimer and fresh solvent is charged. The dynamic MEA degradation between two reclamations has been simulated as two separate Stirred Tank Reactors (STR) and the results from these STRs were fed in the ASPEN process simulation to compute the overall material and energy balance, and predict the gaseous emissions from the absorber and stripper, while rest of the plant operated normally.

Since the source of the oxidative and thermal degradation data was from experiments performed and kinetic models developed by Uyanga and Davis, it was assumed that the steady state emission data generated from ASPEN will be a representation of Uyanga's and Davis's results.

In case of coal fired ultra supercritical (CFUS) power plant, the results from ASPEN based process simulation showed a significant reduction in emission of amine vapour and ammonia from the absorber tower due to inclusion of cooling and water washing.

In case of natural gas combined cycle (NGCC) power plant the flue gas stream had lower concentration of CO_2 and therefore lean gas leaving the absorber showed a lower temperature rise than in the case of coal fired plant. Cooling of lean gas (at the exit of absorber bed) prior to washing was therefore considered to be impractical. The estimated emissions of MEA degradation products were comparable but the ammonia emission was lower than that predicted in the case of coal fired ultra super critical plant. The lower emission of ammonia for NGCC is attributed to a lower degree of degradation of amine due to smaller rise in the absorber temperature.

It is to be noted that the actual emission from a PCC unit will depend on several factors such as operating conditions, flue gas composition, equipment material and additives. Some of these factors such as the operating conditions have been taken into account in the process simulations, but the impact of flue gas impurities from the power plant, such as fly ash or the impact of interaction with the material of construction of the PCC unit has not been taken into account. Only published reaction pathways in the literature have been considered. This has perhaps resulted in an underestimation of the range and concentration of the MEA degradation products in the CO_2-lean flue gas. Hence there is a need to validate the predicted emissions. Currently, there is limited industrial emission data reported in the literature. Therefore experimentally measured emissions of various degradation products in an industrial scale unit will be required to assess the validity of the simulated results presented in this report.

Emissions of Nitrosamines

A few studies have reported the emissions of N-nitroso compounds at different levels from the MEA solvent based CO_2 capture operations. In order to simulate the emission of nitrosamine (in general), the ASPEN process modules were adjusted to include dimethyl-nitrosamine ($C_2H_6N_2O$) from the ASPEN databases into the process stream composition. This nitrosamine was considered in the lean MEA solution and its vapour phase. As a starting point, the calculations for vapour phase were performed for CFUS as well as NGCC power plants. The emission of this nitrosamine in the form of fine droplets was then calculated on the basis of assumed 0.13 m^3 liquid carryover per million m^3 of gas stream. Based on this information, we have carried out an assessment of the potential nitrosamine emissions using a very conservative approach where we have estimated that the emission of nitrosamine could be up to 6.21 g/tonne of CO_2 for coal fired ultra supercritical and 68.4 g/tonne of CO_2 natural gas fired combined cycle plants. The predicted higher emissions in the case of NGCC are due to its lower carbon content which results in a lower CO_2 capture rate from a higher flue gas flow rate. In other words the flue gas produced from coal has more CO_2 than that produced from the natural gas as C/H ratio of coal is higher than the C/H ratio of natural gas. The higher flow of flue with lower CO_2 content results in a higher specific volatilisation of NDMA than in the case of CFUS. By choosing NDMA (a highly volatile generic representative of nitrosamine) it was possible to estimate a maximum possible level of nitrosamines emission from the PCC unit. The results should not be considered as an exact emission of nitrosamines but should be considered as a highest possible level of emission in case nitrosamines formed are as volatile as NDMA. There is an urgent need for a more detailed assessment of the emissions of nitrosamines under realistic conditions.

Processes for minimising emissions

The exit gas streams of CO_2-lean flue gas and carbon dioxide from the PCC plant could contain amine and its degradation products in fine droplet as well as vapour form. Therefore droplet and vapour separation processes are required to capture all emissions from the PCC plant. In this study mainly the processes and equipment for removal of emissions in the exit gas streams are considered.

Considering separation of gases and fine droplets (of liquid) from exit streams, scrubbing, cooling, adsorption and mist elimination processes, which are fairly matured in industry, seem to be suitable approaches for the emission control. According to the literature reviewed, there is not much published on the emission control methods for PCC as the emissions from amine processes appear to be genuinely a new concern in the industry and it is expected that in future more sophisticated methods will be developed to capture emissions from the amine processes.

The flow scheme used in the simulation of MEA based CO_2 capture plant refers to the conventional process where only single stage washing is used. The water washing section after an absorber column is conventionally a one stage process, as these plants are optimised primarily to reduce costs and not emissions. As a result the concentration of amine builds up in the wash water and restricts the recovery of amine due to poor partitioning of amine between the gas phase and the amine contaminated wash water. In this situation a significant amount of amine can be entrained either in droplets or as vapour with the CO_2-lean exhaust gas. Provision of sufficient amounts of fresh wash water is necessary, however all of the water recovered from the stripper or regenerator condenser should be completely recycled to minimise the fresh water consumption.

As reported in the literature, the advanced scrubbing includes more than one stage of counter current washing of the treated flue gas with cold water which is, for instance, recycled from the condenser of the regeneration tower. The recycled water has significantly lower levels of amine and therefore it is quite effective as scrubbing medium, as reported in the literature. The recycling of refluxed water enables washing with large quantity of water to ensure lower concentration of amine in wash water. The water collected in the succeeding stage (upper) is supplied to the water washing in preceding stage (lower). Therefore final washing always maintains a very low concentration of amine and ensures a high extent of extraction of amine. According to the literature, the concentration of amine in the exhaust of CO_2-lean gas could be brought down from 25 ppm for single washing stage to around 8 ppm for three washing stages and multiple stages could be used to further reduce the concentration.

The multiple-stage washing requires low concentration of amine in the wash water at lower temperature to keep the vapour pressure of amine low and this requires a large flow of wash water. Large volumes of water flow could result in large equipment size and costs. Moreover, contacting gases with cold water will trap only those gases which are either soluble in water or condensed at cold water temperature. For example, ammonia is non-condensable at the operating temperature of the wash water but it is quite soluble in water. The solubility of ammonia in water could be increased by cooling and acidification of water. An acid wash technique involving protonation and stabilization of amines and other alkaline degradation products in the solution has been developed. In this technique the water washed flue gas is washed with acid solution at pH around 3-6. The acid aqueous solution is recycled through the acid washing zone to keep a relatively higher concentration of amine salt. A bleed, either continuous or in batch, is sent to a reclaimer to recover amines. The reclaimer could either be a thermal one with or without alkali injection, an ion exchange or a dialysis system, which recycles amine but removes ammonia from the recycling streams. The acid used for washing may be either organic (e.g. formic acid, carbonic acid, citric acid) or inorganic (e.g. sulphuric acid, phosphoric acid, nitric acid). It is to be noted that the use of inorganic acid may further oxidise MEA and produce a stable salt. On the other hand the organic acid may not be destructive to MEA, ammonia etc., and may form amide which could be easily decomposed separately with an inorganic acid such as sulphuric acid to recover the organic acid.

According to the literature reviewed, with single stage cooled water washing, the MEA concentration in the flue gas was reported to be reduced from 55-100 ppm down to 0.7 ppm. Ammonia concentration was reported to be about 30 ppm (wet) measured by FTIR and about 0.4 $\mu g/Nm^3$ of N-Nitrosomorpholine was detected in the flue gas as illustrated in a published patent (WO2010102877-A1). When sulphuric acid was added to reduce the pH of recycling water below 6, the MEA concentration in flue gas was dropped below detection limit which was reported to be around 0.05 ppm. Ammonia concentration decreased below 1 ppm and no N-Nitrosomorpholine was detected in the emitted flue gas.

The addition of acid wash is more effective than three water wash stages because acidic pH enhances the solubility of MEA and its degradation products which are generally weak bases. The mechanism of solubility enhancement by acid is not reported in the literature and it is possible that acid neutralises amine and its degradation products and forms neutral salts. This makes room for fresh dissolution of amine and its degradation products.

UV methods for the destruction of amine particularly nitrosamines have also been developed but they need to be demonstrated at pilot scale. It should be noted that the methods of analysing low concentrations of chemicals and their detection limits were not disclosed in the literature. It is more likely that the detection limits of these methods were lower than the concentrations reported in the literature.

Dissolved CO_2 (carbonic acid) at slightly higher pressure could be sufficient to absorb all amine. When carbonic acid is used the recovery of ammonia and amine could be performed without addition of alkali and by simply boiling off the liquid from acid wash and separating ammonia and CO_2 in a fractionating column.

Adsorption could be used to capture amine and its degradation products. However, adsorbents need to be developed or optimized. The greatest advantage of adsorption processes are their low energy requirements, practically no moving parts, no chemical or water usage.

Cooling could be used for condensable vapours but it is seen as an energy intensive process for deep removal of compounds at low concentration levels.

The scrubbing technology with suitable number of water as well as acid wash stages could also be easily retrofitted into the existing PCC plants with the installation of a separate scrubber unit. Adoption of adsorption technology for capturing emission may require further research and development. Cryogenic processes are well proven at industrial scale but technology is not suitable for non-condensing compounds such as ammonia.

The conventional method of capturing entrained fine droplets of liquid involves use of demisters or mist eliminators, which work on the principle of coalescing fine droplets entrained in gas phase in such as way that they are not re-entrained into the gas phase. The mechanism of coalescing could be: (1) by directly impinging onto surface, (2) by allowing the fine droplets (<5 µm) to diffuse through very narrow passage of dimensions smaller than their mean free path due to Brownian motion, (3) by reducing the velocity of the droplets below their terminal settling velocity and intercepting them with static surface

A number of demisters are commercially available and the review of their performance data indicates that the Swirl Mist Eliminator (SME), which works on the principle of impingement achieved with cyclonic swirling of the fluid, offers a better separation of fine droplets at significantly lower pressure drop than the other demisters. Brownian and wire mesh demisters can also give good separation efficiency but they are susceptible to saturation and Brownian demister offers a higher pressure drop. The SME offers drainage channels isolated from main stream flow to some extent eliminate the possibility of saturation.

Health Safety and Environmental (HSE) Regulations for Chemical Emissions

Emissions of various pollutants from industries are regulated by standards and limits to reduce or control the potential impacts of pollutants on human health and the environment. These industries are required to regularly report on their emissions as per their licence agreements to operate. The identification and quantification of major emissions and the reporting of these values to the appropriate authority are considered as a core activity to demonstrate the environmental performance of the plant.

Emissions from PCC plants may contain chemical substances that are toxic or may have detrimental effect on the environment. Consequently, industrial-scale PCC systems will be subject to pollution mitigation regulation. Most countries have legislations that regulate emissions of common pollutant species which are often referred as the criteria pollutants for monitoring the level of pollution in the environment. These criteria pollutants are ozone, carbon monoxide, sulphur dioxide, nitrogen dioxide, lead and particulate matter that are commonly found in the air. The levels of these pollutants in the environment are monitored and regulated based on their impact on human health and/or environment. The limits set to minimise the impact on human health is called primary standards and the limits set to minimise impact on the environment and property is called secondary standards. Currently, very little is known about the health risks related to amines and their degradation products which could be emitted from PCC unit.

In addition to the criteria pollutants there are a large number of other toxic materials that are of concern globally. In the United States, more than 180 substances have been classified as hazardous air pollutants (HAPs) and similar lists have been developed in many other countries. Some of the compounds that have been identified as potential atmospheric emissions from PCC plants are classified under HAPs. The available health, safety and environmental (HSE) regulations that may be relevant to the emissions from amine-based PCC processes are examined in this section. This involves identification of various emissions, assessment of their permissible levels and examination of HSE regulations to identify if any hazardous emissions are covered by the regulations. While various emissions standards and regulations are discussed, the atmospheric reactions of the chemicals emitted from the PCC unit are not evaluated in this report.

Existing Environmental Regulations

Ambient air quality standard is intended to protect general population from air pollution whereas occupational limits are designed to minimise the exposure of individuals in the work-place. Because of the wide range of industrial chemicals in use, occupational exposure standards exist for many materials, whereas ambient guidelines usually apply to a much smaller range of common hazardous pollutants (mostly the criteria pollutants).

The existing air quality standards do not generally include any of the compounds likely to be associated with PCC emissions. However, there may be broader legislative requirements for industry to reduce all emissions as much as possible. In the EU, for example, the Directive on Integrated Pollution Prevention and Control is intended to minimise industrial pollution. This Directive does not specify emission limits but rather requires that when member states issue operating permits to individual installations, appropriate limits are set according to Best Available Techniques. Similarly, the United States has federal regulations that require industry to eliminate or minimise emissions of the identified HAPs. These more general regulations are very likely to affect the operation of amine based PCC plants

Since there are currently no ambient air quality standards relating specifically to most of the potential PCC emissions, there have been some investigations aimed at developing suitable emission criteria. For example, guidelines for exposure to amine compounds have been suggested by the Norwegian Institute of Public Health. According to these guidelines the exposure limits for MEA, piperazine, AMP and MDEA are 10, 5, 6, and 120 μg m^{-3}, respectively. The maximum exposure limit of 0.3 ng/m^3 was recommended for nitrosamines and nitramines and it may be possible that these limits may be further lowered in future.

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Atmospheric emissions can lead to deposition of certain materials, and potential subsequent eutrophication and acidification of land and waterways may be produced. Accordingly, some guidelines specify emission limits to protect vegetation (e.g. usually limits for NO_2 and SO_2). The WHO Guidelines are expressed as critical levels (CLE) which are defined as concentrations above which adverse effects to plants or ecosystems begin to become apparent. The current CLE for ammonia is 8 μg m^{-3} as an annual mean; however, this value has recently been criticised as being too high. In a study of the effects of ammonia on vegetation, Cape et al[22] found evidence from field observations in Europe that significant damage to vegetation occurs at levels well below the 8 μg m^{-3} CLE. They suggest therefore that 1 μg m^{-3} is more suitable for NH_3.

In Europe as in other parts of the world, transboundary pollution is an important environmental issue and is currently addressed by the 1979 Geneva Convention on Long-range Transboundary Air Pollution. This convention includes a number of protocols intended to cover specific pollutants. The 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (Gothenburg Protocol) seems to be relevant to PCC process. In response to this protocol the European Union has issued Directive 2001/81/EC that set limits for the amounts of pollutant species that can be emitted in individual countries. This directive is designed to reduce emissions of SO_2, NO_x, volatile organic compounds (VOCs), and NH_3. Different countries have different emission limits for these pollutants. Since SO_x and NO_x are also captured in the PCC process the limits set for ammonia and VOCs may be applicable to the emissions from PCC plant.

On the basis of reported emission from the PCC plant the ammonia emission seems to be below the upper limit set by various European countries. For example, in a study reported for a pilot plant operating with a lignite fired power generation plant in Germany, NH_3 emissions were measured to estimate MEA emissions. This study suggested that between about 0.09 and 0.16 kg of NH_3 was emitted per tonne of CO_2 captured. Assuming that all of this CO_2 is to be captured in amine-based PCC plants, emissions would be between 117 and 205 kt NH_3 per annum from all the plants in Germany. This represents about 5 % of the annual combined ceiling emissions of 4294 kt of NH_3 for all the PCC plants in the 27 EU countries. Although this represents a relatively small component of European NH_3 emissions, local nitrogen loads near PCC plants may be adversely affected as well. PCC emissions must be considered in the context of continuing efforts in Europe to significantly reduce emissions of NH_3 and other pollutants.

Many of the potential components of PCC emissions are subject to existing Occupational Health and Safety (OHS) legislation in various countries throughout the world. Consequently, amine-based plants will need to have sufficient emissions control systems to ensure that these standards are met.

It should be noted that at this stage, the composition of amine PCC emissions is largely speculative. Measurement of actual flue gas emissions may reveal a significantly different suite of compounds and a further reassessment of emission limits will be required.

New PCC Amine Systems and their Emissions

Amino acid salt solutions have relatively fast rate of CO_2 absorption, higher CO_2 selectivity, high stability towards oxygen, very low vapour pressure, high biodegradability and favourable binding energy but lower CO_2 absorption capacity than MEA solution. Due to these favourable properties, the amino acid salts have been deployed for commercial scale acid gas removal processes in the past, such as the Alkazid process. Recently, with the increase in interest in PCC, Siemens and BASF have developed new amino-acid based processes for CO_2 capture from power stations. As reported in the literature, these processes produce an insignificant amount of degradation products and have lower emissions to the exiting flue gas.

Aqueous ammonia process has also been claimed, in the literature, as an effective separation with potentially low emissions. Despite the fact that ammonia is toxic and corrosive, considerable attention has been drawn to aqueous ammonia (AA) based process. The main attractions as claimed in the literature are ammonia's estimated 3 times more CO_2 uptake capacity, relatively higher stability, no interference from SO_x and NO_x on the ammonia capture efficiency, and less corrosive nature as compared to MEA. Researchers are currently trying to reduce ammonia losses and emissions. It is important that the performance of ammonia process is thoroughly evaluated to ascertain the operating costs, energy consumption and emissions prior to any construction of commercial scale plant is considered.

Both amino acid salt and aqueous ammonia processes seem to have an insignificant extent of solvent degradation and the base case emissions of ammonia is reported to be below 1 and 10 ppm, respectively. There is no report on any other degradation products (than ammonia) formed in these processes. On application of acid wash the emissions from these processes could be brought down to near-zero. UV methods may not be suitable for these processes as there is no report on nitrosamine emissions from these processes. However, acid treatment process, recirculation or disposal of acid and salt have to be further studied in the laboratory prior to implementation at larger scale.

1 INTRODUCTION

The post combustion capture of carbon dioxide (PCC) from the exhaust gases of the coal and natural gas fired power station, is the most important process for the carbon dioxide capture and storage (CCS) objectives. Since the PCC process is applied as an end-of-the pipe emission control measure, it can be applied to any industrial processes which emit carbon dioxide at near-ambient pressure. A variety of carbon dioxide separation technologies, such as selective membranes, sorption in liquid or on solids, cryogenics, electrochemical methods etc. are currently in various stages of development. However, the separation by amine based solvents is one of the most promising technologies for reducing emissions of CO_2, particularly from carbon intensive processes such as natural gas reformers, natural gas and coal fired power stations. While considerable effort has been invested so far to demonstrate this technology as a feasible option available to the power industry, little attention has been given to the potential emissions of amine based solvents and their degradation products which may be harmful to human health and the environment. These potential emissions raise concerns which require rigorous scientific evaluation prior to widespread implementation of amine based CO_2 capture technology. This will enable appropriate improvements in the technology to be made so that human health and the environment are fully protected from the any adverse impacts.

It is anticipated that the operation of amine-based CO_2 capture plants may emit some new pollutants arising from the amine process for CO_2 capture in addition to typical base-line emissions from natural gas and/or coal combustion. These emissions are likely to result from three major pathways:

(1) physical to and evaporative loss of amine and its degradation products into the gas streams exiting absorber and stripper,
(2) discharge of heavy metal and heat stable salts in the liquid waste streams, and
(3) fugitive emission during plant operation and handling of chemicals, and potential accidental releases.

According to the literature, amongst several likely degradation products of amines and amine vapours, compounds such as nitrosamines and nitramines that have potential to be hazardous to human health and the environment, have to be considered in the emission control strategies. The fates of these compounds in the environment need to be studied to evaluate the overall impact of these compounds and the products arising from their chemical transformation. Some of the compounds associated with PCC such as MEA and some other amines have been used throughout industry for many years and their toxicological effects have been the subject of investigation previously. Some anticipated degradation products also have documented health effects but in general the effect of long-term exposure of people to low levels of these materials is not well understood. Because of this some recent studies have reviewed the known toxicological data for potential PCC emission products with the view to establishing appropriate exposure limits[3,4]. However, it should be realised that at this stage, the nature and quantities of substances that will actually be emitted from a full-scale PCC facility are largely speculative.

This report evaluates the emission of MEA and the expected major degradation products and identifies shortcomings of the existing PCC amine technology. The report briefly reviews various compounds expected to be emitted from the process, describes various available emission control methods and then evaluates their suitability for the existing MEA and other amine based PCC technologies. While various emissions standards and regulations are also discussed, the atmospheric reactions of the emitted chemicals and effect of various inhibitors and additives for the solvents are not evaluated in this report.

2 EMISSIONS FROM PCC PROCESS TO THE ATMOSPHERE

The assessment of atmospheric emissions from amine-based CO_2 capture unit is required to determine the potential impacts of all gaseous and liquid emissions from the unit on human health and surrounding environment. The assessment of these emissions includes identification and quantification of all significant pollutants that are likely to be emitted from the unit.

The emissions from the CO_2 capture units are related to the vaporisation and entrainment losses of amines and their degradation products from the top of the absorber and stripper. Currently, there is a lack of published and validated information about the types and concentration of such of pollutants which are likely to be emitted from the MEA based CO_2 capture units. Therefore, the aim of the current task is to estimate the emission of various pollutants by simulating a CO_2 capture unit based on MEA solvent. This simulation was based on the available literature information on possible MEA degradations during the CO_2 capture process.

The MEA solvent was specifically chosen for simulating the emissions from the proven conventional PCC process as MEA based process appear to be used until alternate solvents become available. Some improved solvents are already being deployed but the existing small-scale units are still predominantly MEA based. For example the Trona unit based on ABB Lummus technology uses a 15-20w% aqueous MEA solution without inhibitor and Fluor Econamine technology uses a 30w% aqueous MEA solution with inhibitors for oxidative degradation and corrosion. Therefore considering MEA as a generic base case solvent was a logical choice for this simulation study.

2.1 Basis and assumptions for simulation

MEA appears to be the preferred solvent by many technology developers at present. The reason for this preference could be its known performance with natural gas sweetening process. Although the extent of degradation of solvent will depend on operating conditions and the type of amine used the strategies and methods to minimise the emissions related to various amine solvents may not be drastically different. With appropriate optimisation and modifications, these emission control methods and strategies could be applied to any of the amine based post combustion carbon capture processes.

Figure 1 shows a generic process flow scheme for the aqueous MEA based post combustion CO_2 capture (PCC) process that formed the basis for the ASPEN process simulation presented in this report. The process flow scheme that was originally produced by Fluor Daniel Ltd and used in the IEA GHG published report[1] has also been used in this study.

The CO_2 capture process releases CO_2 lean flue gas to atmosphere from the top of the absorber. During this process, chemical compounds are produced as a result of amine degradation reactions occurring in the absorber and possibly in the stripper. Most of these products continue to recycle in the unit while fractions of others such as amines (different from the parent amine), ammonia, aldehydes, carboxylic acids, acetamide, oxazolidone (OXA), 1-(2-hydroxyethyl)-2-imidazolidone (HEIA), N,N'-di(hydroxyethyl)urea (DHU), N-2-Hydroxyethylamine (HEEDA), diethanolamine (DEA), nitrosodimethylamine (NDMA), N-nitrosodiethanollamine (NDELA) etc. are also likely to be released to the atmosphere either in vapour form, depending on the phase equilibrium in the system, or in the form of fine liquid droplets, depending on the dynamics within the column and demisters. For example, carboxylic acids are likely to form heat stable salt and may not be volatile but may be emitted as heat stable salt dissolved in fine droplets of liquid in the same way as salt is present in air around oceans.

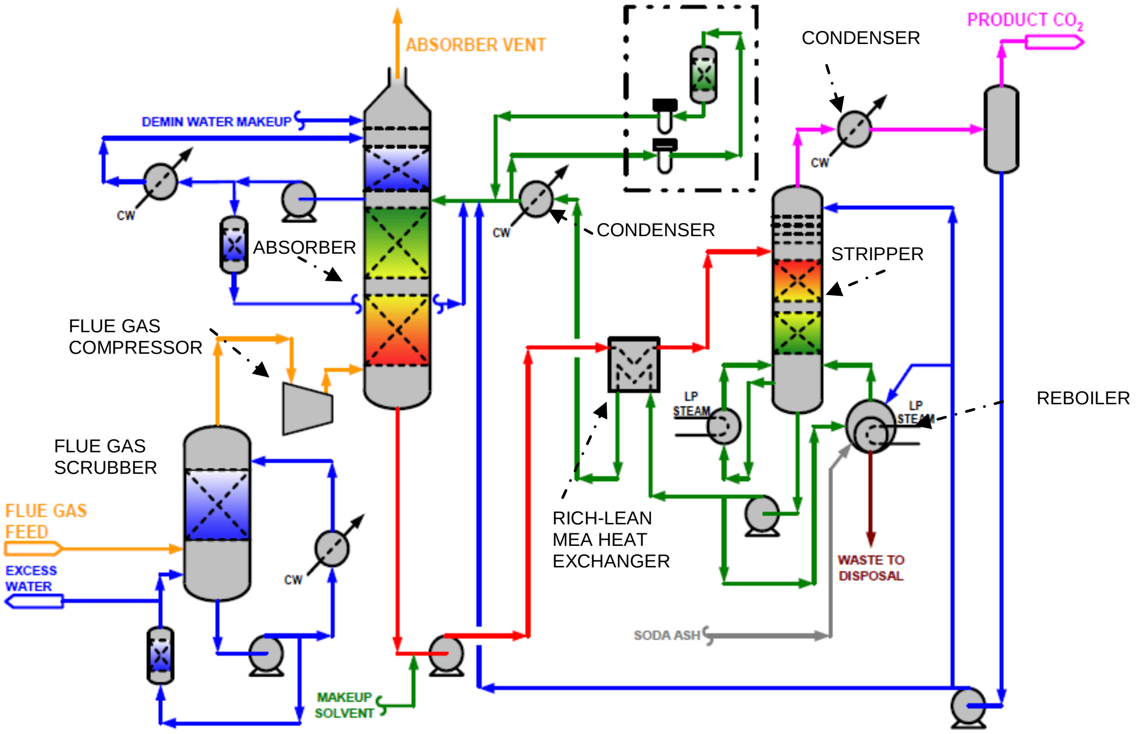


Figure 1 Standard amine based PCC process flow scheme

Ideally, the operating conditions at the top section of the absorber are optimised to minimise the concentrations of these components present as vapour in the exiting CO_2 depleted flue gas emitted from the absorber to the atmosphere. The amount released would depend on the vapour pressure of the gas and liquid constituents and temperature of the absorber. However, some MEA and other produced degradation products may be entrained in droplets exiting with the CO_2 depleted flue gas leaving the absorber.

In the current study, ASPEN-Plus based process models have been used to predict emissions of MEA and its degradation products emitted from MEA-based CO_2 capture units (CCUs). These simulations were carried out to predict emissions from two separate CO_2 capture units which are deployed to treat flue gas generated from a) a coal fired ultra-supercritical (CFUS) power plant and b) a natural gas fired combined cycle (NGCC) power plant. These CCUs were assumed to be operated with 30% w/w aqueous MEA solvent. The operating conditions for the CCU, CFUS and NGCC power plants have been based on the conditions specified in the published IEAGHG report[1], which also includes a detailed description of the capture process for the CFUS and NGCC power plants. The flue gas characteristics and CCU conditions considered for this study are summarised in Table 1.

As shown in Table 1, the SO_2 concentration in the feed flue gas from the CFUS power plant was assumed to be around 10 mg/m^3 in accordance with the upstream flue gas desulphurisation plant specifications. About 200 mg/m^3 of NO_X, with 95%v/v NO and 5%v/v NO_2 were assumed to be present in the flue gas after desulphurisation. In the case of NGCC power plant, SO_2 and NO_2 concentrations were assumed to be around 0.5 mg/m^3 and 20 mg/m^3, respectively as reported in the IEAGHG report[1].

Similar operating conditions were assumed for CCU operated in conjunction with the NGCC and CFUS plants (Table 1). For example, temperatures at the flue gas inlet of the absorber, bottom of stripper, and the lean amine solvent inlet of the absorber were assumed to be at 50^oC, 120^oC and 35^oC, respectively. The CO_2 loading of lean amine solvent was assumed to be at 0.2 mole per mole of MEA. The CO_2 loading of rich amine was around 0.5 mole per mole of MEA. However, the CO_2 capture efficiencies were assumed to be 87.5% for the CFUS power plant and 85% for the NGCC power plant, as referred in the IEAGHG report[1].

Table 1 Assumed characteristics of feed flue gas and CO_2 capture unit (CCU) conditions used for the simulation

Main operating conditions:	**CFUS Power**	**NGCC Power Plant**
Flow Rate (Tonnes/hr)	2973	4733
Temperature (^oC)	50	101
Pressure (kPa)	102.3	102.3
Composition:		
O_2 (Mole %)	4.3	12.5
CO_2 (Mole %)	12.4	4
H_2O (Mole %)	12.2	7.8
N_2 (Mole %)	71.1	75.7
SO_2 (mg/m3)	10	0.5
NO_X (mg/m3)	200	20
CCU conditions:		
Absorber inlet temperature (^oC)	50	50
Stripper bottom temperature (^oC)	120	120
Lean amine solvent inlet temperature at absorber (^oC)	35	35
CO_2 loading with lean amine (mole/mole of MEA)	0.2	0.2
CO_2 capture efficiency (%)	87.5	85
Demineralised and cooling water temperature (^oC)	12	12
Maximum temperature of cooling water (^oC)	19	19

The ambient conditions for the capture unit were set as per the IEAGHG report[1], for example, demineralised and cooling water inlet temperature was considered at 12 ^oC and the maximum rise in cooling water temperature was assumed to be 7 ^oC.

The process simulation assumed the CO_2 absorber to have 32 theoretical stages whereas the solvent regenerator (stripper) was assumed to have 38 theoretical stages. A high number of theoretical stages were deliberately used to get a smooth temperature profile and achieve a maximum likely rise in temperature along the absorber and stripper. This was used to study the effect of maximum temperature rise on the degradation of MEA. For real design and construction purposes the columns should be further optimised.

Both the absorber and the stripper were assumed to operate according to chemical kinetics with mass transfer considerations (ASPEN Rate-Sep Models). The electrolyte Non-Random Two Liquid (NRTL) model from ASPEN's property data bank was used to track the ionic species generated during the CO_2 absorption/regeneration process and determine the overall physical properties of various process streams.

The following reversible chemical reactions were assumed to be possible in the absorber.

$$MEA + CO_2 + H_2O \Leftrightarrow MEACOO^- + H_3O^+ \quad .....(1)$$

$$2H_2O \Leftrightarrow H_3O^+ + OH^- \quad ....(2)$$

$$CO_2 + OH^- \Leftrightarrow HCO_3^- \quad ....(3)$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+ \quad ....(4)$$

$$MEA + H_3O^+ \Leftrightarrow MEAH^+ + H_2O \quad ....(5)$$

Reactions 1 and 3 were assumed to be kinetically controlled whereas the other reactions were at equilibrium.

The major pathways leading to solvent loss during the CO_2 absorption process were assumed to be linked to the:

- Entrainment of fine droplets of liquid in the treated gas due to hydrodynamics
- Pick up of vapours by the treated gas due to thermodynamics (vapour-liquid equilibrium)
- Degradation of solvent and loss as liquid degradation products

The physical liquid entrainment losses from the absorber are usually minimised by a suitable mist eliminator (usually Chevron type) between the absorption section and the wash section of the absorber, and a wire-mesh mist eliminator at the top of the absorber. Generally, it is difficult to estimate this loss accurately since it is influenced by a number of competing factors governing hydrodynamics within the absorber. However, a detailed literature search for the unit operating data for the MEA based CO_2 capture units reveals that in a well managed unit this loss could be as high as 0.03 kg per tonne of CO_2 captured[5]. The Handbook from Gas Processors Suppliers' Association[6] quotes liquid carryover from various types of mist extraction devices as 0.01 to 0.13 m^3 per million m^3 of gas stream. Actual liquid carryover in a plant will be very much dependent on the column packing, demister design and the operating conditions. It is possible that there may not be any emission during normal operation of a column provided with a demister which is specifically optimised to eliminate all emissions. However, even in such an optimised design a situation is possible where the column and demister are flooded with liquid due to some malfunctioning. In this situation fine droplets are very likely to be emitted and we have considered the possibility of this worst case operating condition. Since it was impossible to predict a realistic liquid carryover figure, the highest possible level of liquid carryover has been assumed to estimate the highest level of emission from the column. The highest value in the range from the Handbook of Gas Processors Suppliers' Association was also used to estimate physical carryover of wash water in the treated gas that leaves the wash section. From the assumed quantity of entrained wash water and its chemical composition, the actual physical entrainment losses of MEA solvent and its degradation products were calculated. The chemical composition of the entrained wash water was considered to be same as that of the wash water circulating inside the wash section at steady state operation.

The vapour phase carryover of MEA in the treated gas can be minimised by keeping the gas temperature sufficiently low and washing it with cold demineralised water. This loss can be estimated theoretically since the vapour pressure of MEA, its solubility in water, lean gas composition and carbon dioxide concentration (if any) in wash water at a given absorber operating temperature and the contact time are the only influencing factors.

2.1.1 MEA Degradation

Thermal degradation at temperature higher than 100 °C and oxidative degradation in the presence of oxygen are responsible for the degradation of MEA solvent used for CO_2 capture.

MEA undergoes degradation in the presence of CO_2 at temperature around 120°C in the reboiler and the stripper, The degradation products such as Oxazolidone-2, 1-(2 Hydroxyethyl) imidazolidone-2 (HEIA), N-(2-Hydroxyethyl)-ethylenediamine (HEEDA), N-(2-hydroxyethyl)-diethylenetriamine (Trimer), N-(2-hydroxyethyl)-triethylenetetramine (Polymer), and Cyclic Urea of Trimer are produced according to the reactions shown by equations 11-16. The rate of formation of these products is believed to be function of temperature, CO_2 loading and MEA concentration. The ethylene amine derivatives (HEEDA, Trimer and Polymer) could be decomposed or regenerated in situ to release MEA. Moreover, these compounds promote corrosion of the process equipment, especially when the partial pressure of CO_2 is high.

In addition to thermal degradation, MEA undergoes oxidative degradation due to presence of oxygen in the flue gas. The reaction of dissolved oxygen with MEA in aqueous solution is known to produce mainly NH_3, and aldehydes (α- amino acetaldehyde H_2NCH_2COH , acetaldehyde, formaldehyde etc), which with further reactions with oxygen turn into corresponding acids as described in the following reactions[5]:

$$C_2H_7NO + 0.5O_2 \Leftrightarrow H_2NCH_2COH + H_2O \qquad (6)$$

$$2C_2H_7NO + O_2 \Leftrightarrow 2CH_3COOH + 2NH_3 \qquad (7)$$

$$C_2H_7NO + 1.5O_2 \Leftrightarrow 2HCOOH + NH_3 \qquad (8)$$

$$C_2H_7NO + 2O_2 \Leftrightarrow HOCOCOOH + NH_3 + H_2O \qquad (9)$$

These aldehydes can further react with oxygen to form carboxylic acids, such as formic acid, glycolic acid, acetic acid, and oxalic acid. These carboxylic acids can also react further with MEA to form heat-stable salts, or with other degradation products to form a wide variety of high molecular weight products. These degradation products will end up in the reclaimer without having great potential to be emitted to the air. Other degradation products also could be formed, such as glycine, and it is still not clear yet if the direct or indirect oxidation of MEA produces carcinogenic compounds such as nitrosamines and nitramines.

Corrosion of the process equipment with these acidic products produces organo-metallic salts. The extent of salt formation depends on the concentration of amine and oxygen in the solution, temperature and pressure. However, Thitakamol et al[5] have shown that the formates and acetates comprise nearly 90% of heat stable salts (HSS) .

The following empirical power-law kinetic model was developed by Uyanga et al[7] to predict the rate of MEA degradation during CO_2 capture from power plant flue gas streams.

$$-R_{MEA} = 0.00745 * e^{-45258/RT} * (MEA)^{1.9} * (CO_2)^{-0.3} \{(SO_2)^{3.4} + (O_2)^{2.8}\} \qquad (10)$$

Where, $-R_{MEA}$ is the rate of O_2- and SO_2-induced degradation of MEA (mol l^{-1} h^{-1})) and R the gas constant (8.314 J mol^{-1} K^{-1}). [MEA], [SO_2], [O_2], and [CO_2] are the respective concentrations of MEA, SO_2, O_2, and CO_2 (presented in units of mol l^{-1})

In order to simplify the process simulation, it was envisaged that the oxidative degradation of MEA will eventually end up in formic acid and ammonia as the final degradation products. Alternatively, kinetic parameters for all parallel reactions shown by equation 6 to 9 could have been incorporated into the model and this was considered as a rather complicated method. Moreover, the kinetic data for such reactions was not found in the literature.

The kinetic equation (10) was used in the ASPEN modelling for simulating only formic acid and ammonia formation reactions at equilibrium within the absorber and stripper to account for the oxidative degradation of circulating amine solution.

In the current study, the thermal degradation of MEA was modelled in ASPEN using the reaction mechanism described by Davis[8]. The following chemical reactions, described by the thermal degradation pathways, may have occurred in the solution. The kinetic parameters of these reactions are illustrated in the table below.

$$MEA + CO_2 \xrightarrow{k_1} C_3H_5NO_2 - N_2 \ (Oxazolidone) + H_2O \tag{11}$$

$$MEA + C_3H_5NO_2 \xrightarrow{k_1} C_4H_{12}N_2O \ (HEEDA) + CO_2 \tag{12}$$

$$HEEDA + Oxazolidone \xrightarrow{k_2} C_6H_{17}N_3O \ (Trimer) + CO_2 \tag{13}$$

$$Trimer + Oxazolidone \xrightarrow{k_3} C_8H_{22}N_4O \ (Polymer) + CO_2 \tag{14}$$

$$HEEDA + CO_2 \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} C_5H_{10}N_2O_2 \ (HEIA) + H_2O \tag{15}$$

$$Trimer + CO_2 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} C_7H_{15}N_3O_2 \ (Cyclic\ Urea) + H_2O \tag{16}$$

Kinetic parameters of various thermal degradation reactions

Rate Constant	**Pre-Exponential Constant (L/day/mole)**	**Activation Energy (Kcal/mole)**
K_1	1.05E16	34.4
K_2	2.15E16	33.3
K_3	3.28E15	31.5
K_4	3.58E16	33.0
K_{-4}	4.47E15	32.6
K_5	3.65E15	31.3
K_{-5}	4.56E14	31.3

It should be noted that the presence of oxidative and thermal degradation products in the lean amine solvent may have the potential to affect the solvent properties such as surface tension, viscosity and density which affect the droplet size distribution and the extent of physical carryover of solvent droplets in the treated gas. These degradation products might also be responsible for foaming which may result in increase the pressure drop across the absorber and enhance the droplet as well as the vapour phase emissions.

2.1.2 Estimation of Degradation Product Build-Up

The MEA-based post combustion CO_2 capture units extract a slip stream from the solvent circulation loop (between 0.5 to 3 w% of the solution flow) either continuously or every 3 to 4 weeks and pass it through the reclamation steps to maintain a required low concentration of solvent degradation products in the circulating solution. With the continuous reclaiming it is possible to maintain a very low concentration of degradation products in the MEA solution but with the batch operation of the reclaimer the concentration of degradation products in the MEA solution will periodically rise between two consecutive reclamation operations. In this study the batch operation is considered to allow a maximum possible degradation of MEA to take place in a given period between two reclamations. This was a deliberate attempt to estimate the worst case effect of MEA degradation on the process emissions.

Since the ASPEN Rate-Sep simulation package provides material and energy balance for CO_2 capture unit under the steady state operating conditions, there is no direct way to estimate periodic or dynamic degradation of MEA solvent and build up of its degradation products that is likely to occur in the real operation of a PCC unit. In order to estimate periodic degradation of MEA using the ASPEN simulator, the steady state CO_2-saturated or CO_2-rich amine stream leaving the absorber and the steady state CO_2-unsaturated or CO_2-lean amine stream leaving the stripper were duplicated as feed streams for two separate Stirred Tank Reactors (STR) in a separate ASPEN simulation.

The reactor processing CO_2-rich amine stream was assumed to operate at the average pressure of the absorber and stripper and at the temperature of the stripper inlet feed stream. This reactor accounted for the oxidative degradation reactions only. The residence time for CO_2-rich amine stream in this reactor was varied to determine the build up of oxidative degradation products with time. Since these degradation products are not reversed in the stripper, it was assumed that in a real capture unit environment as MEA continues to circulate between the absorber and stripper, its oxidative degradation over time is best approximated by the extent of degradation product formation in the Stirred Tank Reactor as its residence time varies. Thus, from time, t = 0, to time, t = 6 weeks, oxidative degradation was simulated using the rate expression given by Uyanga et al[7] described previously. It is to be noted that residence time in the simulated CSTR was varied from 0 to six weeks to allow formation of various degradation products and no predetermined inventory of compounds and their concentrations was considered. The maximum concentration of degradation products was dependent upon the reactants and the period of the reactions carried out in the CSTR.

In order to model thermal degradation of MEA, the Stirred Tank Reactor with CO_2-lean amine stream leaving the stripper was assumed to operate at the stripper bottom pressure and the re-boiler outlet temperature. By using this highest temperature of the re-boiler outlet, the maximum possible concentration of thermal degradation product in the emissions to the atmosphere was estimated assuming that there will be maximum degradation at the highest temperature in stripper. An argument could suggest use of an average temperature to have an average emission rather than an overestimation. However, it is to be noted that this does not seem to be an overestimation as in the real situation the degradation reactions will continue to progress until the maximum temperature (reboiler outlet temperature of 120 ^oC) is attained and it will not stop at the average temperature of the reboiler or stripper.

The residence time for the CO_2-lean amine stream in this reactor was varied to determine the build up of thermal degradation products with time. Since these degradation products are not reversed in the absorber, it was assumed that in a real capture process environment as MEA continues to circulate between the absorber and stripper, its thermal degradation over time is best approximated by the extent of degradation product formation in the Stirred Tank Reactor as its residence time varies. Thus, from time, t = 0, to time, t = 6 weeks, thermal degradation was simulated using various rate expressions given by Davis[8] described previously. Some of the major degradation products of amines, such as N-(2-hydroxyethyl) acetamide can potentially convert back to its parent amine and carboxylic acid easily through hydrolysis reaction under high temperature and basicity of amine solvent encountered in the stripper. It was not possible to simulate this reaction in ASPEN due to unavailability of appropriate databases. However, the literature data on the formation of acetamide in the absorber and its emission to the atmosphere has been considered in the study.

Since the emissions from the towers are predicted through separate STRs, it was assumed that all units such as heaters, coolers, heat exchangers, absorber and stripper performed at the rated capacity and there was no emission related to their malfunctioning or de-rating. Only gaseous emission from the absorber (and stripper) has been estimated and there was zero effluent discharged from wash water, cooling water or any other stream.

2.2 Simulation Results and Discussion

2.2.1 CO_2 Capture Unit for Coal Fired Ultra supercritical (CFUS) Power Plant

The flow scheme of the CO_2 capture process along with the results from steady state mass and energy balance simulated on ASPEN-plus is shown in Figure 2. The simulation results show the re-boiler heat duty for this capture unit as 3.52 MJ/kg of CO_2. The detailed mass and energy balance at steady state around the CO_2 absorber is further illustrated in Figure 3. It shows that due to chemical reactions during absorption, stream 2 leaving the CO_2 absorber (ABSORBER) has 65^oC temperature and it needs to be cooled down to 45^oC to reduce the wash tower (WASH) load. This cooling load is approximately 166 MW_{th} and it is picked up by water cooled heat exchanger (B8 in Figures 2 and 3). In the conventional flow scheme without intercooler the emission will be entirely dependent on the absorber and stripper temperatures and these temperatures and associated emissions could not be controlled by any control strategy. Therefore an additional after-cooler or condenser has been installed to arrest vapours at the absorber exit. The cooling after absorber (*i*) condenses some of the vapours and (*ii*) returns the condensate at 40 ^oC back to the absorber. This way vapour emission from the absorber could be controlled without affecting the steady state performance of the absorber. The other alternative, i.e. to operate the absorber at lower temperature, was considered to be more energy intensive.

This implies that in a real PCC unit, the absorber will need to have an after-cooler or condenser to reduce atmospheric emissions of MEA and its degradation products. It should be emphasized that while simulating steady state CO_2 absorption, care was taken to have zero effluent discharge from the wash tower. Circulating wash water in the wash tower was bled into the lean amine solvent stream to an extent that the concentrations of MEA and MEA degradation products in the recirculating wash water were maintained below about 300 ppmw (3×10^{-04} mass fraction), according to the simulation performed on ASPEN.

Figure 4 and 5 show vapour phase emissions of MEA and other chemicals in mg per tonne of CO_2 captured at the absorber outlet stream# 2 and at the water wash outlet stream# 30, respectively. A comparison of results plotted in Figure 4 and 5 clearly indicates a significant decrease in the concentrations of MEA, NH_3, HEIA and HEEDA in the CO_2-lean flue gas as a result of water washing. The cooling of CO_2-lean flue gas from the absorber and subsequent water washing seems to be very effective in removing the majority of the emissions which seems to be very high at the exit of the absorber column. These results also indicate that at both the absorber outlet and the wash tower outlet, MEA and its degradation products such as NH_3, Oxazolidone, HEEDA and HEIA, will be present in the gas phase. Carboxylic acids (HCOOH) that are produced during the degradation of MEA are trapped as stable salts in the solvent. The solvent along with the degradation products may be emitted along with the fine droplets if the absorber column and demisters are not operating properly and are flooded with liquid. This droplet emission is not simulated by ASPEN.

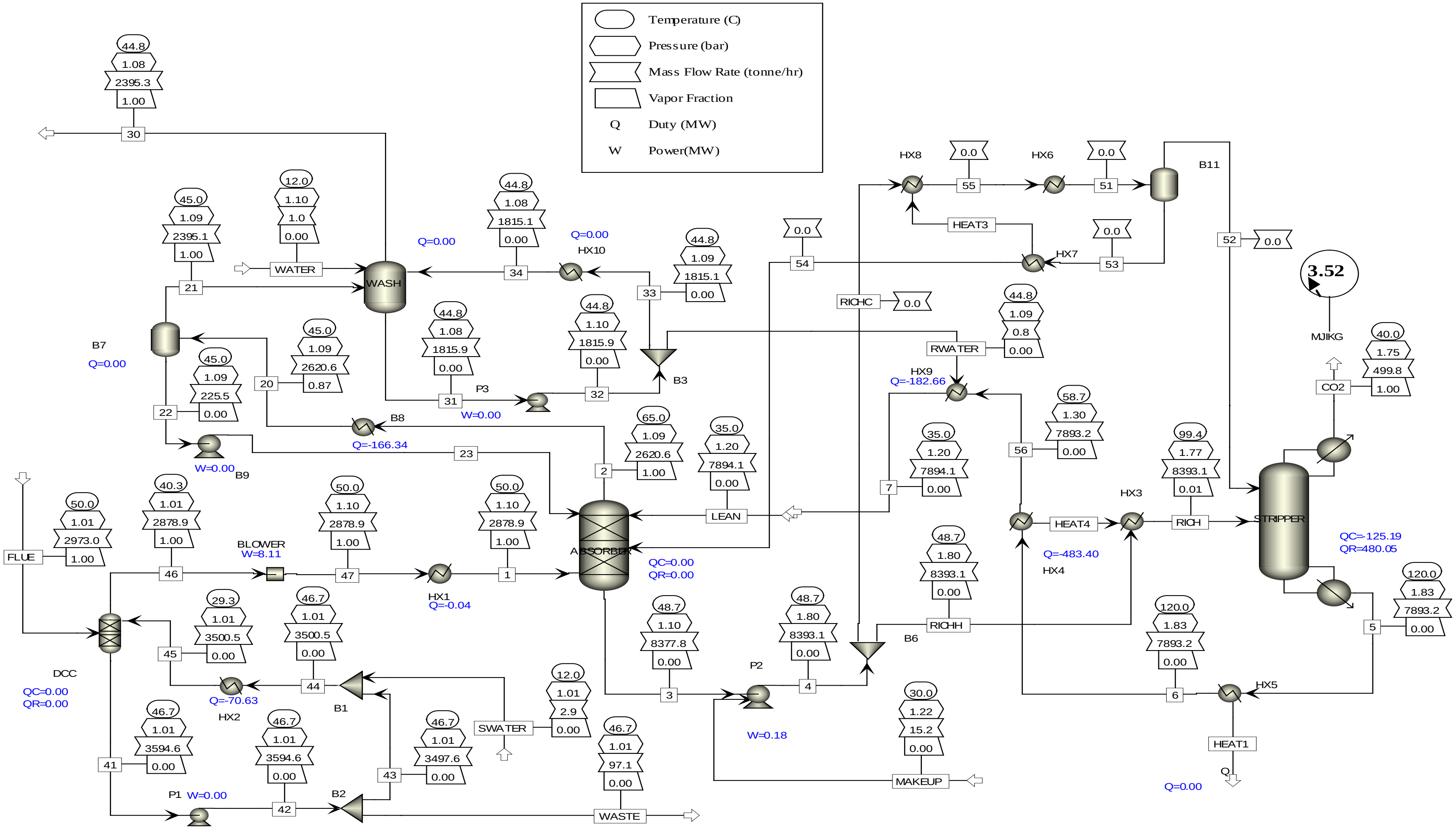


Figure 2 Flow scheme of simulated CO_2 capture unit for CFUS power plant

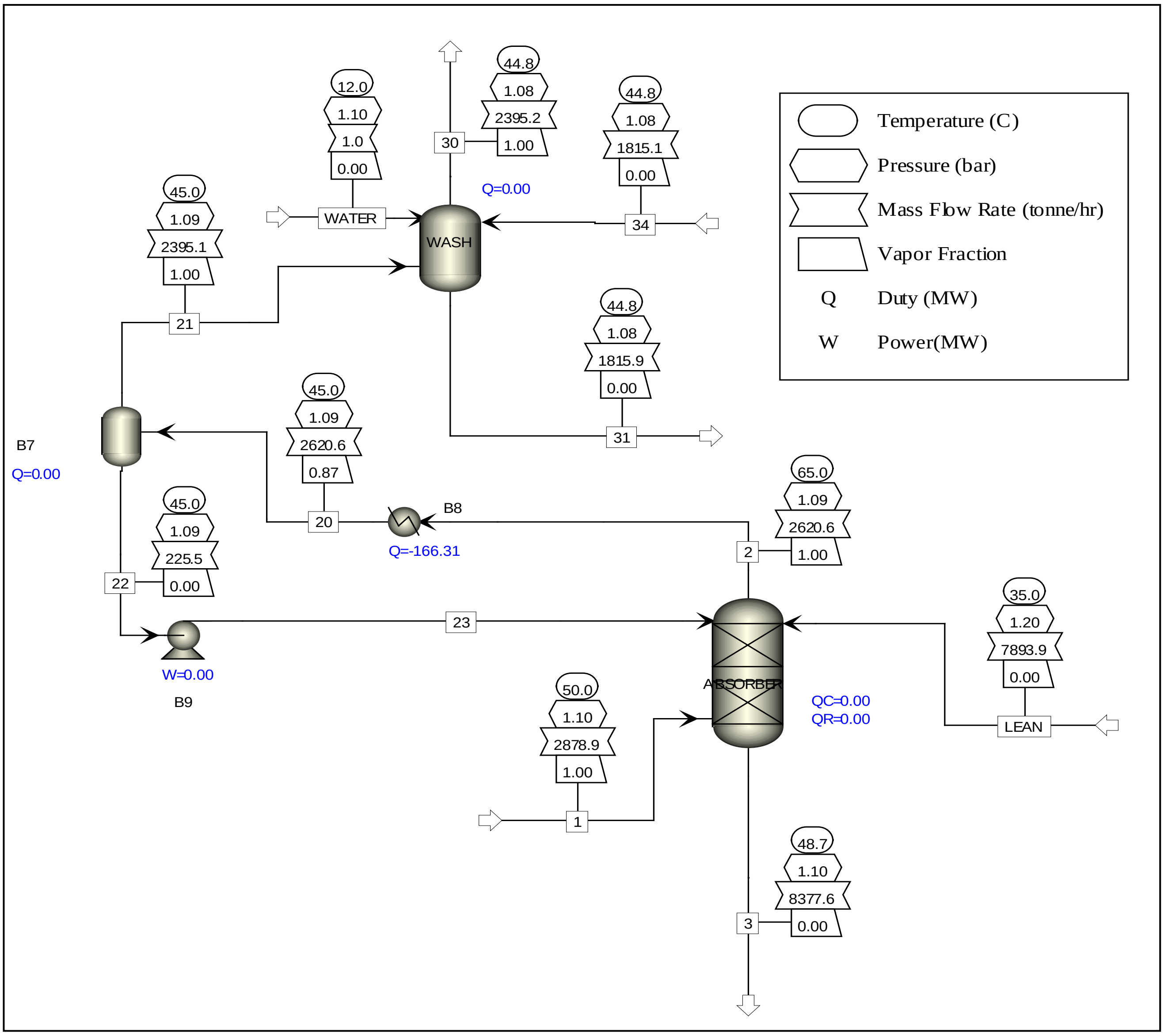


Figure 3 Flow scheme of simulated CO_2 absorber of the PCC process for CFUS power plant

The results at 0th week represent vapour phase emissions of MEA and its degradation products when the PCC unit is operated at steady state with the solvent having completed its first circulation between absorber and stripper. It obviously shows only MEA emission in the gas streams as it represents the situation where the capture unit is operated at steady state without any degradation of MEA.

As solvent continues to circulate, NH_3, heat stable salts, Oxazolidone, HEEDA, HEIA, Trimer, Polymer and cyclic Urea are formed with time. However, only NH_3, Oxazolidone, HEEDA and HEIA appear in gas streams 2 and 30 in Figure 2 in addition to MEA. Whilst NH_3 and HEIA are emitted at practically negligible concentration levels in both streams, MEA emissions are constant and Oxazolidone emissions rise with time. The comparison of results in Figure 4 with Figure 5 clearly shows that cooling of absorber outlet gas and washing it with large quantity of demineralised water in the wash tower minimises emissions of MEA and its degradation products to atmosphere.

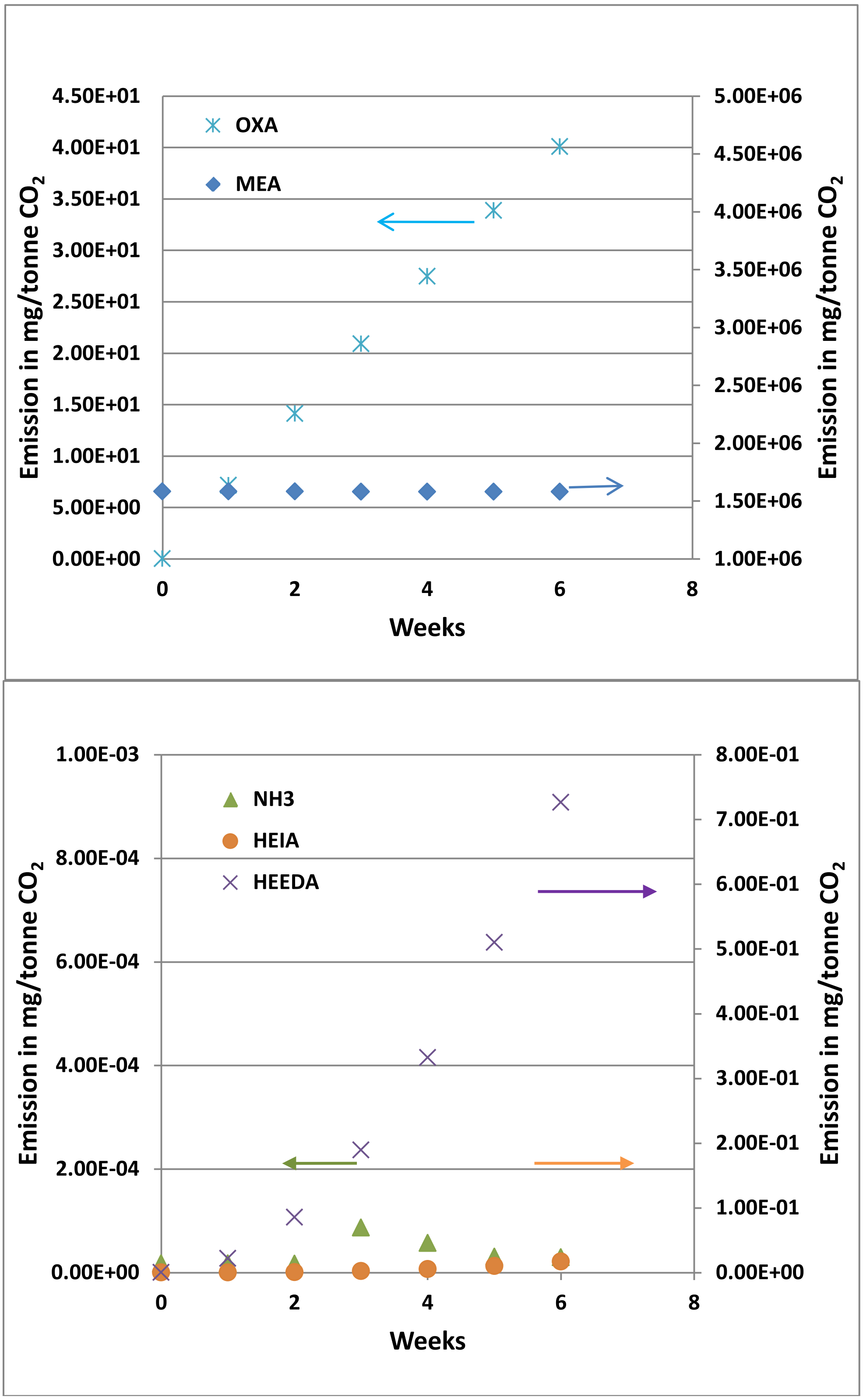
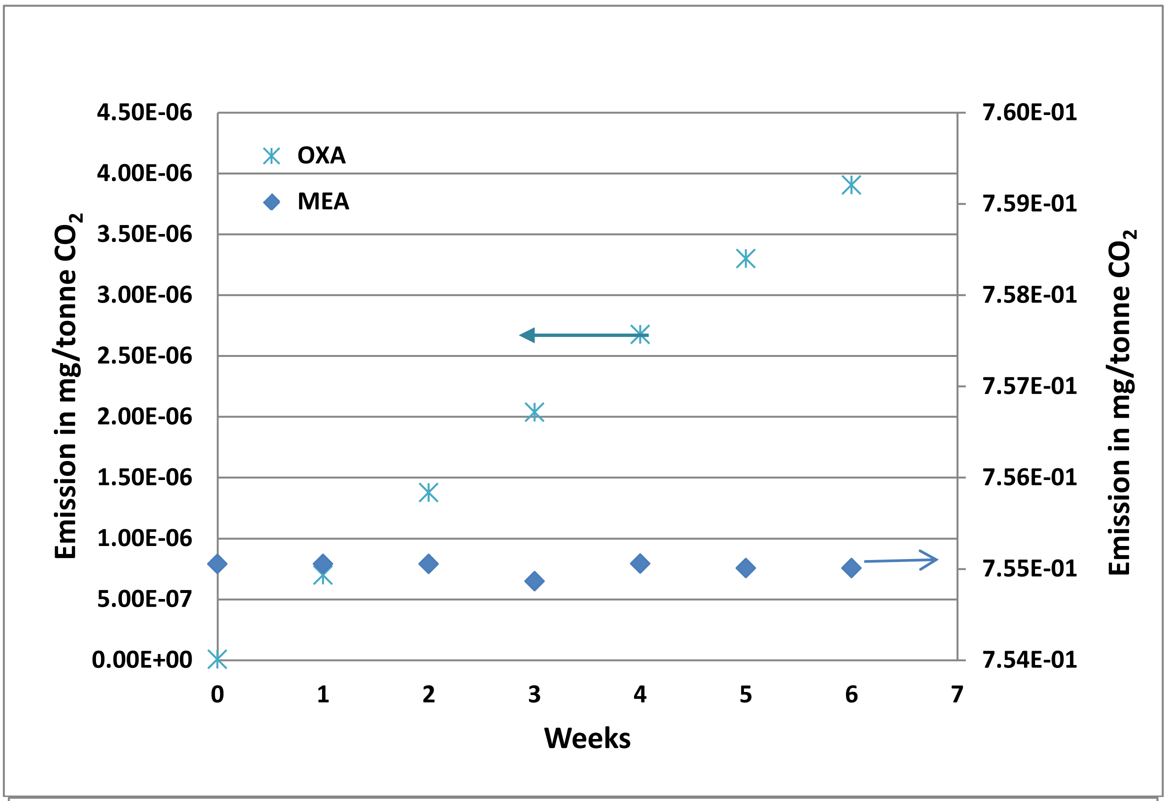


Figure 4 Vapour phase emissions of MEA & degradation products at absorber outlet (Based on ASPEN simulation using oxidative degradation data from Uyanga et al[7] and thermal degradation data from Davis[8])



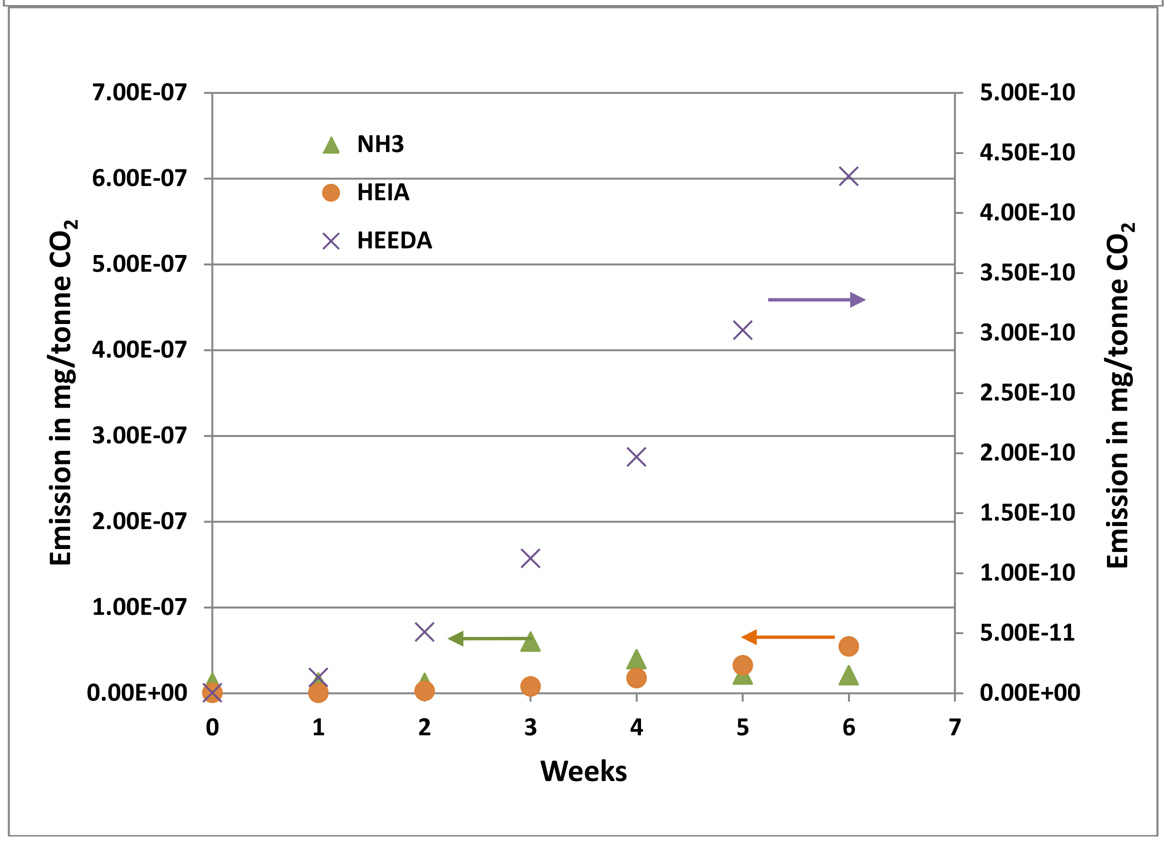


Figure 5 Vapour phase emissions of MEA & degradation products at wash tower outlet (Based on ASPEN simulation using oxidative degradation data from Uyanga et al[7] and thermal degradation data from Davis[8])

Table 2 shows emissions of MEA and its degradation products in the water washed CO_2 lean gas stream at the exit of the wash tower at 45°C. The tabulated results show that the vapour phase emissions of heat stable salts such as HCOOH assumed in this study, NH_3 and various thermal degradation products in the water washed CO_2 lean flue gas stream are practically very low but the MEA emission remains practically constant at 0.76 mg/tonne of CO_2.

Table 2 Vapour phase emissions of MEA and its degradation products in CO_2 lean flue gas after water-wash (mg/tonne of CO_2 captured, based on ASPEN simulation using oxidative degradation data from Uyanga et al[7] and thermal degradation data from Davis[8])

	t =0	**t=1 week**	**t=2 week**	**t=3 week**	**t=4 week**	**t=5 week**	**t=6 week**
MEA	7.55E-01	7.55E-01	7.55E-01	7.55E-01	7.55E-01	7.55E-01	7.55E-01
HCOOH	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Ammonia	1.21E-08	1.21E-08	1.18E-08	6.00E-08	3.95E-08	2.13E-08	2.05E-08
HEEDA	0.00E+00	1.28E-11	5.06E-11	1.12E-10	1.97E-10	3.02E-10	4.30E-10
OXAZOLIDONE	4.75E-09	6.98E-07	1.38E-06	2.04E-06	2.68E-06	3.30E-06	3.90E-06
HEIA	0.00E+00	0.00E+00	2.30E-09	7.50E-09	1.71E-08	3.23E-08	5.41E-08

Table 3 summarises the vapour phase emissions and selected degradation products published by Moser et al[9] and Aas[10] that were observed after absorber and after water wash systems.

Table 3 Vapour phase emissions* of MEA and its degradation products in CO_2 lean flue gas (CASTOR/CESAR Capture Program[9])

Chemicals	**After Absorber (mg/Nm^3 dry CO_2 lean flue gas)**	**After Water Wash (mg/Nm^3 dry CO_2 lean flue gas)**
MEA	0.7	<0.3
DEA	<0.3	<0.2
Formaldehyde	0.7	<0.1
Ammonia	25	20
Methylamine	<0.3	<0.2
Acetamide	<1.0	<1.0

** These data summarised from the pilot plant results published by Moser et al[9] and Aas[10]*

According to our ASPEN based simulation the inclusion of an after-cooler or condenser (B7 in Figure 3) along with a condensate separator (B8 in Figure 3) at the exit of the absorber, which receives condensate from the condensate separator results in a lower vapour phase emission of MEA as compared to published by Moser et al[9], who have measured total MEA loss of about 6 g/tonne due to emission in CO_2 lean flue gas and CO_2 captured under similar operating conditions in a post combustion capture pilot unit producing 7.2 tonnes of CO_2 per day. This PCC unit was linked to a lignite fired power plant at Niederaussem, Germany. Moser et al. also observed practically zero emissions of heat stable salts and other thermal degradation products in CO_2 lean flue gas. However, NH_3 emissions were detected as ranging between 89 to 155 g per tonne of CO_2 (or 27 to 47 mg/Nm^3 of dry CO_2 lean flue gas).

In a recent publication Moser et al reported[11] that MEA loss in a recent test campaign at Niederaussem pilot scale unit was around 0.3 kg/tonne of CO_2 captured. This was significantly lower than the values reported[12,13] for test campaigns at the Esbjerg plant (1.4-2.4 kg/ tonne of CO_2 captured. Moser et al[11] also reported that the consumption of MEA and the measured losses of MEA are caused by emissions and accumulation of degradation products in the solvent shows a good mass balance to confirm the validity of these results of MEA losses.

Our estimates of MEA emissions are lower than the total losses reported by Moser et al, due to two main reasons; (1) Results published by Moser et al corresponds to total loss including emission as well degradation products in the solution phase whereas our simulation results correspond to only emission with the CO_2 lean flue gas, and (2) simulation really does not fully represent all degradation and corrosion reactions that occur in the real system.

The current ASPEN-predicted emission concentrations do not consider the kinetic equations for MEA decomposition to NH_3, but it uses the rate expression developed by Uyanga et al[7] (2007) to simulate the formation of heat stable salts. Moser et al[9] also reported the presence of acetaldehyde (<0.2 mg/Nm^3 dry gas) and acetone (0.5 to 1 mg/Nm^3 dry gas) in the water washed CO_2 lean flue gas in addition to NH_3 as a result of oxidative degradation. Similarly, Aas[10] measured various chemicals present in the CO_2 lean gas at the outlet of absorber and water wash in a post combustion capture pilot unit. Their results as summarised in Table 3 were measured in a post combustion CO_2 capture pilot unit that was operated at a CO_2 production capacity of 1 tonne/hr under the CASTOR/CESAR research program at Dong Energy's Esbjerg based bituminous coal fired power plant. The results published by Aas[10] indicate that the pilot unit was operated in such a manner that the temperature of CO_2 lean flue gas at the exit of the water wash tower was around 45^{o}C.

Much of the available data on oxidative degradation is based on laboratory experiments. The extrapolation of the results should be treated with caution because the dynamics of the laboratory scale experimental conditions differ from those encountered in a pilot or full scale CO_2 capture unit. Appropriate kinetic data on the formation of DEA, formaldehyde, acetaldehyde, acetone, ammonia, methylamine and acetamide were not available in the literature during this study. For these reaction products, it is therefore necessary to rely on data determined in emissions measurements. Using the range of pilot unit emissions data reported by Moser et al[7] and Aas[10] estimated likely concentrations of several compounds in the CO_2 lean gas are given in Table 4. It was assumed that these concentrations might occur in Stream 2 or Stream 21 in the flow scheme given in Figure 3.

Table 4 Estimated concentrations of MEA degradation products in the CO_2 lean gas (dry basis) at the absorber outlet in a PCC plant using 30 w% MEA to capture CO_2 from flue gas of a coal fired power plant

Degradation products*	**Approximate concentration (mg/Nm^3) in dry CO_2 lean flue gas**
DEA[10]	0.3
Formaldehyde[9,10]	0.35
Acetaldehyde[9,10]	0.35
Acetone[9]	0.5
Ammonia[9,10]	27
Methylamine[10]	0.3
Acetamide[10]	0.5

*****_The superscript on the compounds refers to Moser et al[7] and Aas[10] who have claimed emission of these compounds in the CO_2 lean flue gas_.

The degradation products summarised in Table 4 could be present in the vapour phase at the above stated concentration levels in the process stream 21 after water wash section above the absorber of the flow scheme shown in Figure 3.

It is possible that DEA could be produced as a degradation product from MEA or inherently present in MEA as a by-product from MEA manufacturing. In a recent publication Fostas et al[14] have reported formation of up to 50 µg of DEA/g of MEA. However the mechanism and kinetics of MEA degradation is not very certain at this stage therefore it is not possible to predict the level of DEA present in MEA solution. If DEA is somehow present with MEA during the capture process then it is certain that it will also participate in CO_2 capture and its emission to the atmosphere will also vary depending on the extent of its contribution towards CO_2 capture.

Assuming that the capture unit was operated at steady state and solvent was reclaimed at the end of 3rd week after start-up, the likely atmospheric emissions of MEA and its oxidative as well as thermal degradation products were calculated in ASPEN simulation using the data presented in Table 4. The ASPEN calculations involved inserting the concentration of various degradation products as shown in Table 4 into Stream 2 or Stream 21 and normalising the stream flow rate, thus providing estimates of these products after the wash water section in Stream 30 as shown in Table 5. The atmospheric emissions of these degradation products in the droplet phase carryover of wash water from the wash tower was calculated using 0.13 m^3 droplets carryover per million m^3 of CO_2 lean gas stream. Table 5 also shows the results of these calculations.

A thorough examination and evaluation of droplet formation in the absorber and stripper column would require a separate study as there is not much reported information on droplet formation related to MEA solvent based scrubbers. However, droplet entrainment in high pressure gas-liquid separation been subject of study particularly for high pressure processes related to oil refining[15] and the main challenges in these estimations were; (1) determination of minimum flooding point (the minimum distance from the scrubbing surface where demister should be installed for minimum flooding), (2) determination of variation in the height of flooding point with the variation in process dynamics and operating conditions[16].

A mathematical modelling based approach for addressing these challenges is quite useful to identify the presence of liquid as a liquid film and as dispersed droplets above the scrubber bed. The models proposed by Whalley[17], Morud[18] and Chtzikyriakou et al[19] could be useful in predicting overall mass transfer and velocities but these models do not predict droplet size distribution accurately. More complex models illustrated by Patruno et al[20,21] described droplet-size distribution by a droplet-density function. Ambrosini et al's[22] model presents only mean diameter of the droplets but does not account for the statistical variations in the droplet size distribution. Kataka and Ishii[23] modified Paleev and Filipovich's[24] model to describe entrainment and deposition of droplets and estimate overall mass transfer as a global parameter. Sawant et al[25] have found that Pan and Hanratty et al's[26] model underestimates the entrainment at higher pressures but it is reasonably accurate at low pressures. Out of these the more relevant study seems to be by Kataoka et al[27] and Tatterson et al[28] who presented model for droplet entrainment in an air–water system. Fore et al[29] also measured entrainment of droplets distribution in air-water system at higher pressures and Azzopardi[30] reported lack of data in low-surface tension systems particularly at high pressure range. Jakobsen[31] and Patruno et al[32] developed a model to describe droplet breaking, deposition, collision and coalesce under population-balance framework but none of these reported models have been used to describe entrainment of droplets from a liquid which has properties similar to MEA solution with CO_2 . This means the results predicted by these models could not be used to accurately predict the entrainment in absorber and stripper

Table 5 Vapour and droplets emissions to the atmosphere of MEA and its degradation products (CFUC power plant case)

Emissions	**Chemicals Input In Stream 2**				**Chemicals Input In Stream 21**			
	As vapour		**As droplets**		**As vapour**		**As droplets**	
	mg/tonne	**mg/Nm^3(dry)**	**mg/tonne**	**mg/Nm^3(dry)**	**mg/tonne**	**mg/Nm^3(dry)**	**mg/tonne**	**mg/Nm^3(dry)**
MEA	7.49E-01	2.39E-04	4.25E+01	1.36E-02	6.18E-01	1.97E-04	4.25E+01	1.36E-02
Ammonia	6.87E+01	2.19E-02	1.55E+01	7.61E-05	3.58E+03	1.14E+00	7.73E+02	3.81E-03
HEEDA	1.12E-10	3.58E-14	1.99E-09	6.36E-13	1.12E-10	3.58E-14	1.99E-09	6.36E-13
OXAZOLIDONE	2.04E-06	6.50E-10	2.81E-06	8.97E-10	2.04E-06	6.50E-10	2.81E-06	8.97E-10
HEIA	7.50E-09	2.40E-12	1.81E-09	5.78E-13	7.50E-09	2.40E-12	1.81E-09	5.78E-13
TRIMER	0.00E+00	0	0	0	0.00E+00	0	0	0
CYCLIC UREA	0.00E+00	0	0	0	0.00E+00	0	0	0
POLYMER	0.00E+00	0	0	0	0.00E+00	0	0	0
DEA	7.22E+02	2.31E-01	2.61E-02	8.33E-06	7.44E+02	2.37E-01	2.69E-02	8.58E-06
FORMALDEHYDE	9.19E+02	2.93E-01	2.07E-02	6.61E-06	9.36E+02	2.99E-01	2.11E-02	6.73E-06
ACETALDEHYDE	9.78E+02	3.12E-01	1.30E-02	4.15E-06	9.89E+02	3.16E-01	1.31E-02	4.20E-06
ACETONE	1.16E+03	3.72E-01	4.85E-02	1.55E-05	1.20E+03	3.84E-01	5.02E-02	1.60E-05
METHYLAMINE	7.45E+02	2.38E-01	2.33E-02	7.44E-06	7.64E+02	2.44E-01	2.39E-02	7.63E-06
ACETAMIDE	7.53E-04	2.41E-07	4.64E-04	1.48E-07	3.75E-01	1.20E-04	2.31E-01	7.38E-05

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The actual liquid carryover in a plant will be very much dependent on the column packing, demister design and the operating conditions. It is possible that there may not be any emission during normal operation of a column and demister specifically optimised to eliminate all emissions. However, even in such an optimised design a situation is possible where the column and demister is flooded with liquid due to some malfunctioning. Under this situation fine droplets are very likely to be emitted and we have considered a possibility of this worst operating condition. Since it was impossible to predict a realistic liquid carryover figure, the highest level of possible entrainment is considered in the present study and a further study is recommended in this area to accurately determine the droplet entrainment in the absorber and stripper columns.

The production of aerosol is unlikely anywhere in the PCC process as there will be very low concentration of SO_x present in the flue gas after desulphurisation. There are no references indicating the possibility of aerosol formation in the PCC unit. However, in case there are traces of SO_2 and SO_3 present it may produce aerosol in the water scrubbing section upstream absorber but such aerosols will not be able to make their way through the absorber, water wash and demister into the atmosphere. In case there is a possibility of aerosol formation and release into the atmosphere an appropriate demister would have to be installed.

It is also to be noted that the accuracy of mass and energy balance results obtained from ASPEN depends on the convergence error or tolerance considered, and the accuracy of the input data such as MEA degradation data. If the convergence limit is very low and MEA degradation data is accurate then the results obtained from ASPEN are expected to have similar levels of accuracy as that of the source data. However, it is a usual practice to validate ASPEN results with laboratory, bench scale, pilot and demonstration scales prior to full scale process development.

Some authors reported[14] on DEA formation during CO_2 capture by the MEA solvent and in order to account for any emissions related to DEA formation we have included DEA in the MEA solvent phase. However, no reactions to produce DEA from MEA have been considered. The emissions from two possible scenarios where (a) DEA did not capture CO_2, and (b) DEA did capture CO_2, were studied as shown in Table 6 and 7, respectively.

The main reason for considering these two scenario to cover all the possible MEA degradation routes therefore products reported[14] in the literature. Some authors reported formation of DEA[14] and reaction with CO_2 and other reported no DEA formation. We presume that DEA may be produced but it may or may not be effectively contributing towards CO_2 capture due to its very low proportion as compared to MEA but it may have some contribution in terms of emissions. It is also thought that it will be very difficult to confirm the extent of contribution of DEA in capturing CO_2 in the simulation, therefore two extreme cases, with and without reaction with CO_2 were considered.

It is to be noted that methylamine was not considered in out simulation as it was not available in the data base of ASPEN. Moreover, the main objective of the study was to assess possible emission and technologies to eliminate them and it is presumed that the technology that will be suitable of the degradation products simulated will also be able to remove methylamine.

Table 6 shows the range of atmospheric emissions of MEA and its significant degradation products in CO_2 lean gas that leaves the water wash tower of a post combustion CO_2 capture unit that processes coal-fired power plant flue gas using 30% w/w aqueous MEA solution and where DEA did not capture gaseous CO_2.

Table 6 Range of atmospheric emissions of MEA and its degradation products when DEA did not capture gaseous CO_2 (CFUS power plant)

Chemical Emissions	Minimum		Maximum	
	(mg/tonne of CO_2 captured)	(mg/Nm^3 of CO_2 lean flue gas)*	(mg/tonne of CO_2 captured)	(mg/Nm^3 of CO_2 lean flue gas)
MEA	43	0.014	43	0.014
Ammonia	84.2	0.022	4353	1.14
DEA	722	0.231	744	0.237
FORMALDEHYDE	919	0.293	936	0.3
ACETALDEHYDE	978	0.312	990	0.316
ACETONE	1160	0.372	1200	0.384
METHYLAMINE	745	0.238	764	0.244
ACETAMIDE	-	-	0.6	0.0002

It should be noted that Ammonia, DEA, Formaldehyde, Acetaldehyde, Acetone, Methylamine and Acetamide emission levels are predicted at the end of 3rd week of operation of the capture unit when reclamation of the solvent is recommended to reduce the concentration of degradation products in the circulating solution.

Table 7 Range of atmospheric emissions of MEA and its degradation products when DEA in wash water also captured gaseous CO_2 (CFUS power plant)

Chemical Emissions	Minimum		Maximum	
	(mg/tonne of CO_2 captured)	(mg/Nm^3 of CO_2 lean flue gas)*	(mg/tonne of CO_2 captured)	(mg/Nm^3 of CO_2 lean flue gas)
MEA	43	0.014	43	0.014
* Ammonia	1980	0.63	3600	1.14
DEA	-	-	0.14	4.43E-05
FORMALDEHYDE	919	0.293	936	0.3
ACETALDEHYDE	978	0.312	990	0.316
ACETONE	1160	0.372	1200	0.384
METHYLAMINE	745	0.238	764	0.244
ACETAMIDE	-	-	0.6	0.0002

** the high concentration of ammonia with DEA formation could be related to simultaneous degradation of MEA to HEEDA and then to nitrosomorpholine (NMOR) as illustrated by Fostas et al[14] but the exact reason for these results have to be verified.*

Table 7 shows the corresponding results when the reaction of DEA dissolved in wash water with uncaptured CO_2 is taken into consideration.

2.2.2 CO_2 Capture Unit for Natural Gas Combined Cycle (NGCC) Power Plant

Since the NGCC power plant flue gas stream has lower CO_2 concentration compared to that for the coal-fired power plant flue gas stream, the rise in temperature of CO_2 lean gas leaving the absorber is low and it does not warrant cooling prior to washing. Figure 6 shows the simulated flow scheme along with the material and energy balance of the simulated PCC process at steady state. The reboiler heat duty for the capture unit in this case is 3.68 MJ/kg of CO_2 captured. Figure 7 shows the process streams around the Wash Tower. Just as in the case of CFUS power plant, zero effluent discharge from the wash tower has been assumed in the simulation and the circulating wash water in the wash tower was bled into the lean amine solvent stream only to the extent to maintain the concentration of MEA and its degradation products in the wash water.

Figure 8 and 9 show variation in emission of MEA and oxazolidone vapour with time at the outlets of absorber (stream 2) and wash tower (stream 30), respectively. These results are comparable to what we have observed in case of the simulated PCC unit for coal fired ultra supercritical plant and show that at both the outlets, MEA and its degradation products, NH_3, oxazolidone, HEEDA and HEIA, will be present in the gas phase. The results at 0th week show only MEA emission without any degradation of MEA. As solvent continues to circulate the degradation products such as NH_3, heat stable salts, oxazolidone, HEEDA, HEIA, Trimer, Polymer and Cyclic Urea are formed with time but only NH_3, oxazolidone, HEEDA and HEIA appear in gas streams in addition to MEA. Although MEA vapour concentration in stream 2 and stream 30 appears to remain constant with time, the concentration of other chemicals appears to rise until 3rd week and then becomes constant.

Table 8 Emissions (mg/tonne of CO_2 Captured) of vapours of MEA and its degradation products post water-wash

	t =0	**t=1 week**	**t=2 week**	**t=3 week**	**t=4 week**	**t=5 week**	**t=6 week**
MEA	3.62E+04	3.62E+04	3.62E+04	3.62E+04	3.62E+04	3.62E+04	3.62E+04
HCOOH	0.00E+00	1.31E-16	1.46E-15	1.46E-15	1.46E-15	1.46E-15	1.46E-15
Ammonia	0.00E+00	0.00E+00	7.01E-08	7.01E-08	7.01E-08	7.01E-08	7.01E-08
HEEDA	0.00E+00	1.25E-11	4.92E-11	4.92E-11	4.92E-11	4.92E-11	4.92E-11
OXAZOLIDONE	6.85E-09	6.60E-07	1.30E-06	1.30E-06	1.30E-06	1.30E-06	1.30E-06
HEIA	0.00E+00	1.36E-08	2.26E-09	2.26E-09	2.26E-09	2.26E-09	2.26E-09

A comparison of Figure 8 with Figure 9 shows that washing of the CO_2 lean gas (stream 2) leaving the absorber with demineralised water in the wash tower significantly reduces the emission of vapours of MEA and its degradation products.

Table 8 shows the vapour phase emissions of MEA and its degradation products in the water washed CO_2 lean gas stream leaving the wash tower at 50.5°C, which is about 5°C higher than in the case of CFUS power plant (see Figure 2) to account for a slightly higher

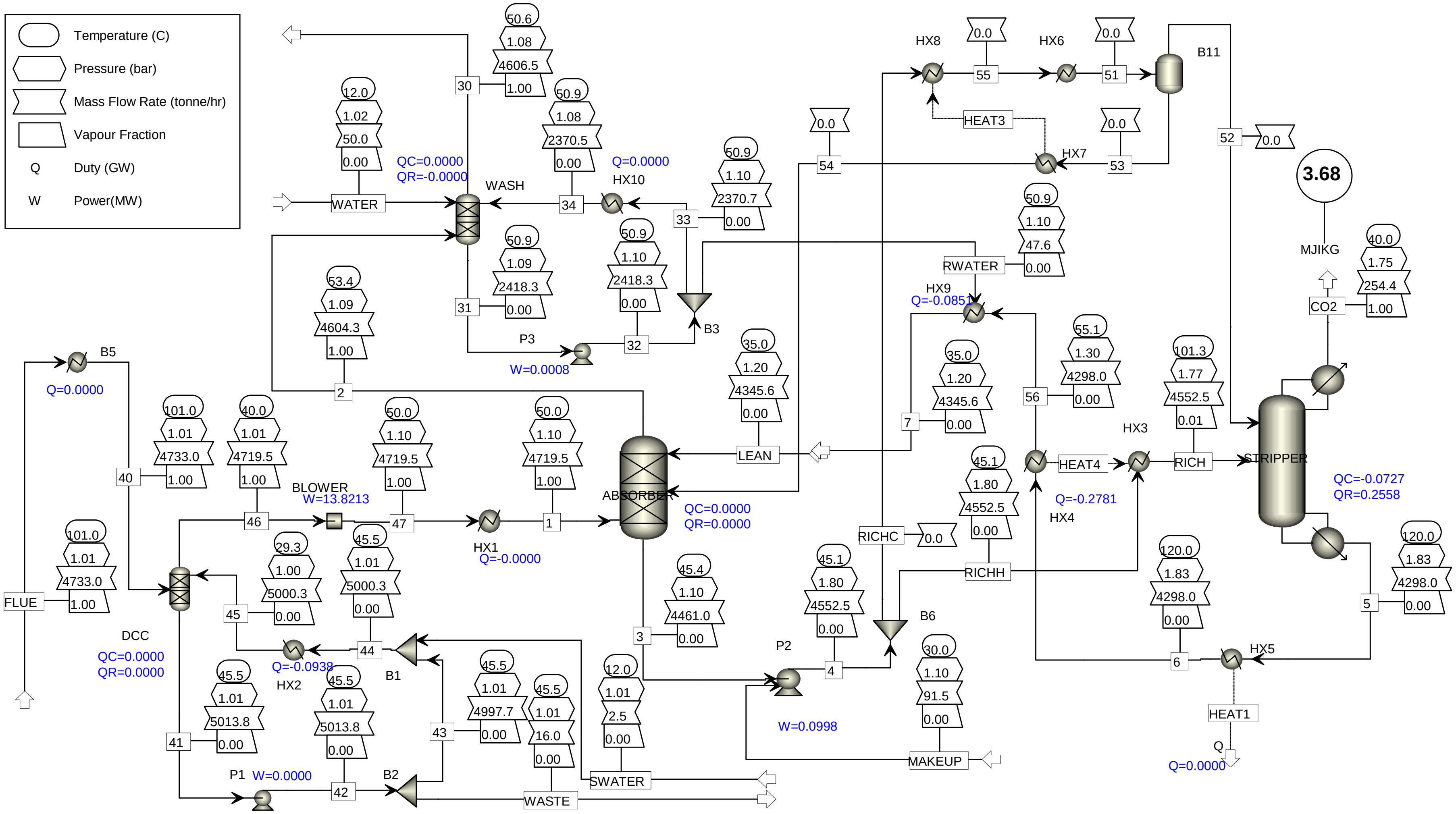


Figure 6 Flow scheme of simulated CO_2 capture process for NGCC power plant

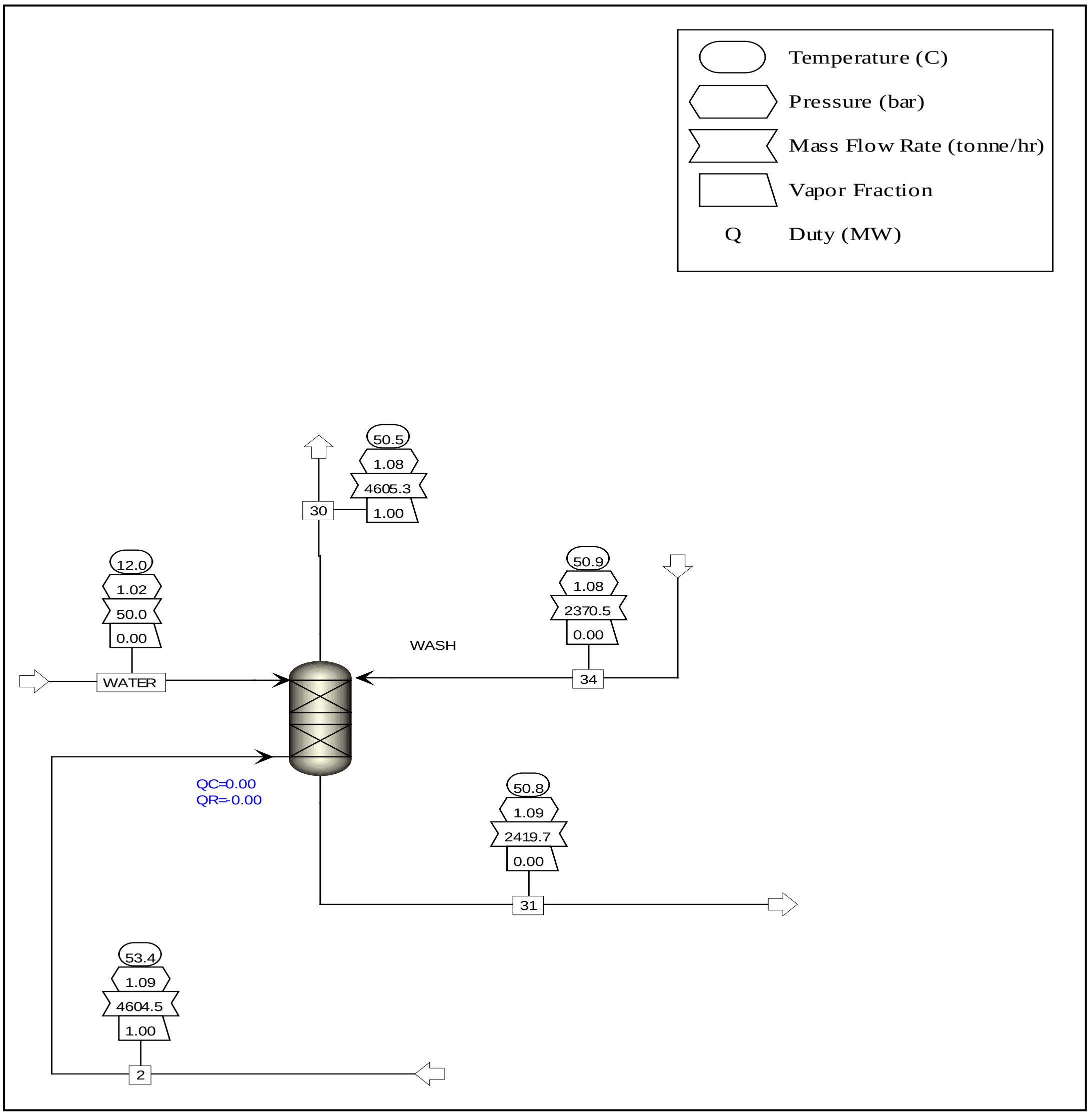


Figure 7 Flow scheme of simulated wash tower of the PCC process for NGCC power plant temperature of the absorber of the PCC unit simulated for NGCC power plant, as reported in the IEAGHG report[1]. It shows that the vapour phase emission of MEA degradation products in water washed CO_2 lean flue gas stream is negligible but MEA emission remains constant at 36.2 g/tonne (or about 158 mg/m^3) of CO_2, according to our simulation. It is to be noted that such emissions are largely dependent on the operating conditions and therefore could vary significantly. It is also important to ensure that the figures compared have the same units as well as denominator, i.e. CO_2 captured, feed flue gas or depleted flue gas etc. It should also be noted that in the case of CFUS, the concentration of HEIA should be more than HEEDA in the vapour phase for NGCC power plant but the Aspen-Plus simulation results show a higher concentration for HEEDA and we could not find a scientific explanation for this anomaly which may be due to some inaccuracy of ASPEN.

For a NGCC power plant of 420 MW_e power generation capacity operating about 8000 hours per year, it amounts to 72.4 tonnes per year of MEA emissions to atmosphere. Veltman et al[33] reported that a MEA based CO_2 capture unit for a 420 MW_e NGCC power plant, operating for about 8000 hours per year, has about 79 tonnes/year of MEA emission.

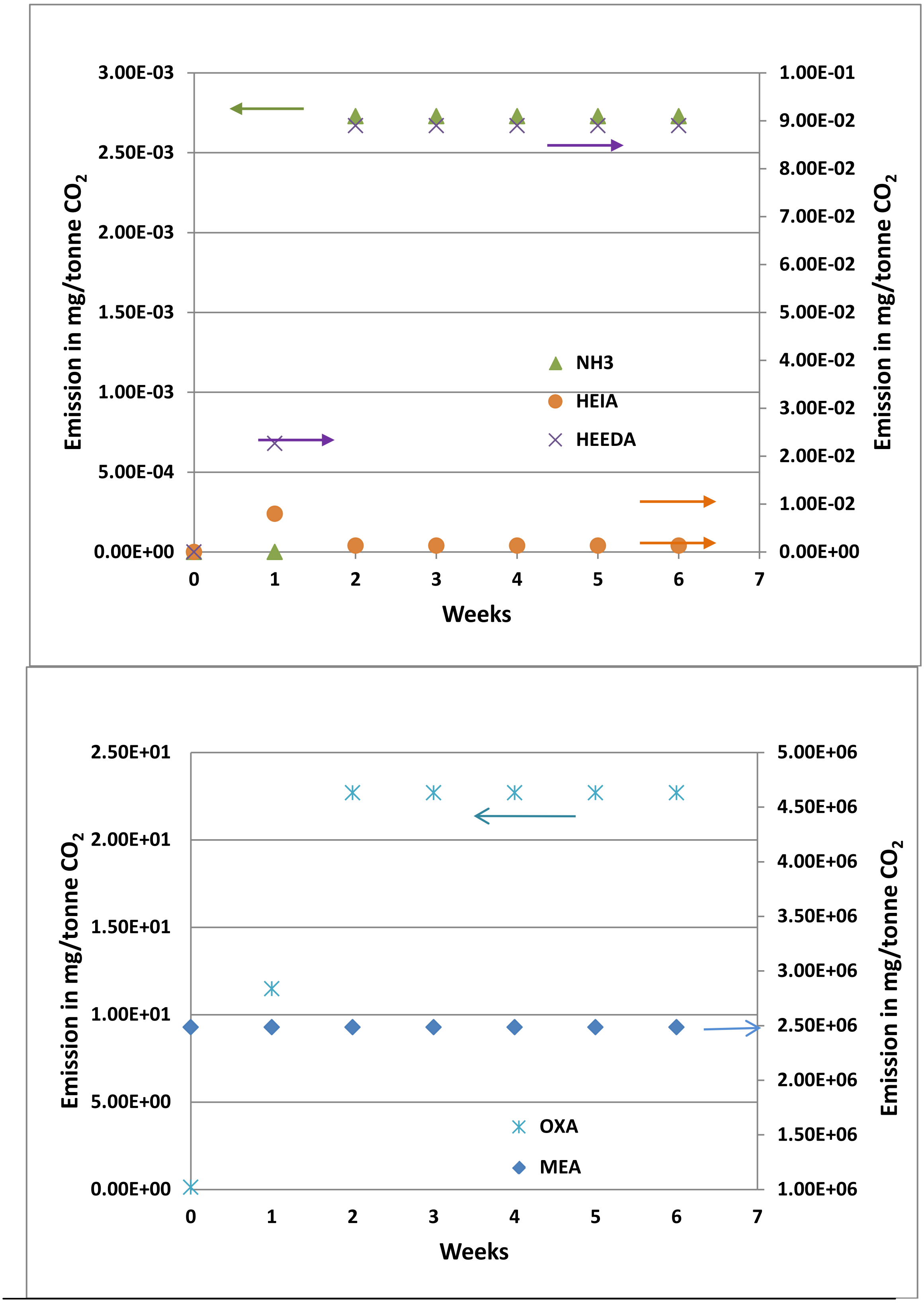


Figure 8 Vapour phase emissions of MEA and degradation products at absorber outlet

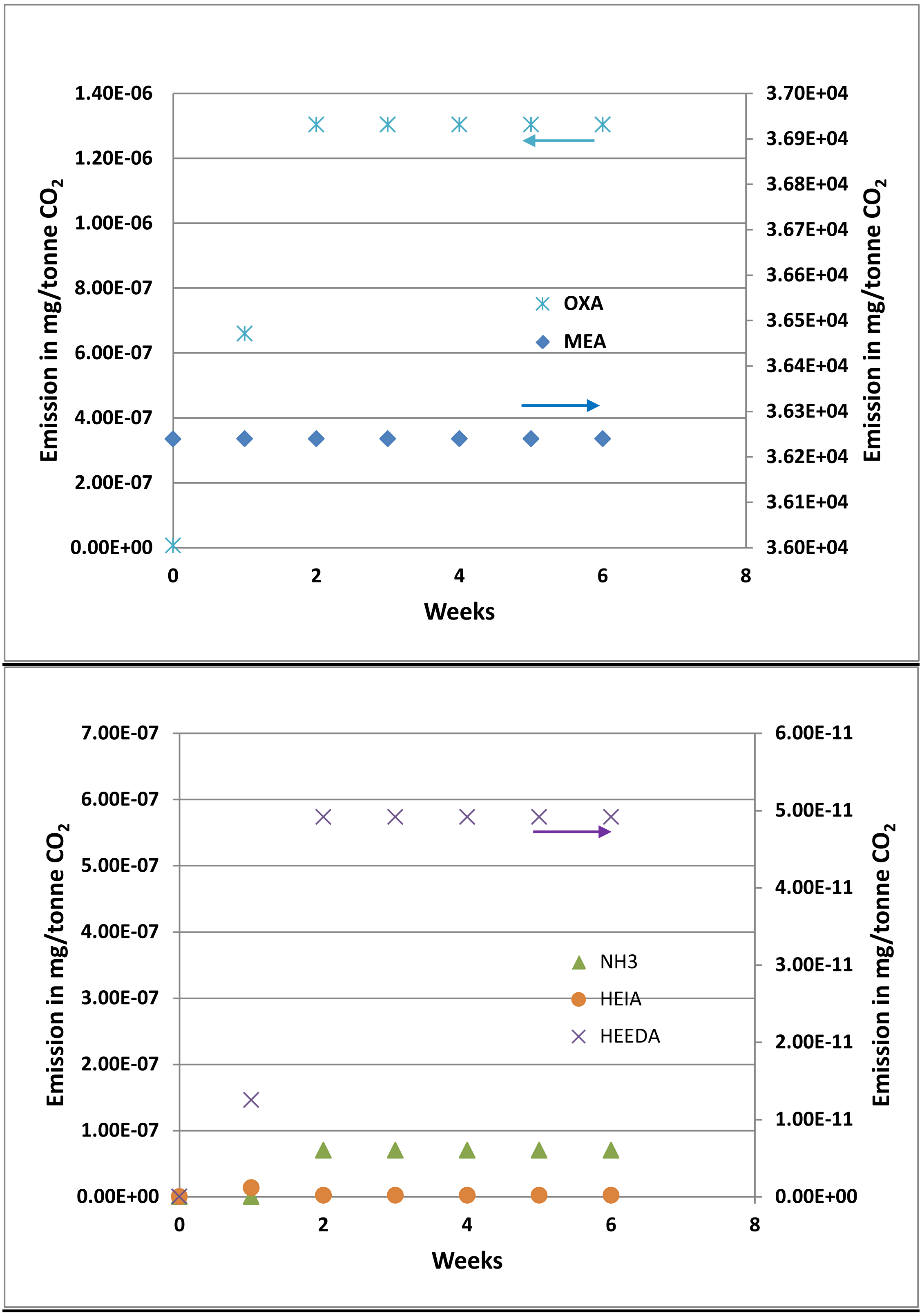


Figure 9 Vapour phase emissions of MEA and degradation products at wash tower outlet

Very low emission of NH_3 were estimated because the current process model does not consider the rate equations for MEA decomposition to NH_3 but shows formation of heat stable salts using the rate expression developed by Uyanga et al[7]. In order to estimate emissions of other degradation products such as DEA, formaldehyde, acetaldehyde, acetone, methylamine, acetamide etc., very limited information on kinetics is available in the literature. Veltman et al[33] reported that about 330 and 210 kg/year (which equates to about 163 and 94 mg/tonne of CO_2 captured based on 365*24*0.95 hours operation of a PCC unit coupled with a 400 MW coal fired power plant) emission of formaldehyde and acetaldehyde, respectively, were possible with water washing of CO_2 lean gas at the exit of the absorber.

If the emission measurements of Moser et al[9] and Aas[10] from capture units linked to coal-based power plants are chosen as the basis, then the emissions of MEA and its degradation products to air after 3rd week of the capture unit operation will be as shown in Table 9. This assumes that DEA generated during degradation of MEA does not participate in the capture process.

Table 9 Emissions of MEA and its degradation products without DEA reactions (for simulated PCC for NGCC power plant)

Degradation products	**As vapour**		**As fine droplets**		**Total**	
	mg/Nm^3 dry CO_2 lean flue gas	**mg/tonne of CO_2 captured**	**mg/Nm^3 dry CO_2 lean flue gas**	**mg/tonne CO_2 captured**	**mg/Nm^3 dry CO_2 lean flue gas**	**mg/tonne CO_2 captured**
MEA	3.13E+00	3.60E+04	2.37E+00	2.74E+04	5.50E+00	6.34E+04
Ammonia	1.36E-03	1.57E+01	1.12E-02	1.29E+02	1.26E-02	1.45E+02
HEEDA	4.21E-15	4.85E-11	1.72E-09	1.98E-05	1.72E-09	1.98E-05
OXA	1.12E-10	1.29E-06	4.38E-07	5.05E-03	4.38E-07	5.05E-03
HEIA	1.94E-13	2.24E-09	2.54E-11	2.93E-07	2.56E-11	2.95E-07
TRIMER	6.27E-20	7.23E-16	2.83E-11	3.27E-07	2.83E-11	3.27E-07
CYCLIC UREA	0.00E+00	0.00E+00	0.00E+0	0.00E+00	0.00E+00	0.00E+00
POLYMER	0.00E+0	0.00E+00	0.00E+0	0.00E+00	0.00E+00	0.00E+00
DEA	2.54E-01	2.93E+03	8.93E-06	1.03E-01	2.54E-01	2.93E+03
FORMALDEHYDE	3.14E-01	3.62E+03	6.53E-06	7.53E-02	3.14E-01	3.62E+03
ACETALDEHYDE	3.26E-01	3.76E+03	3.91E-06	4.50E-02	3.26E-01	3.76E+03
ACETONE*	4.22E-01	4.87E+03	1.53E-05	1.77E-01	4.22E-01	4.87E+03
METHYLAMINE	2.60E-01	3.00E+03	7.60E-06	8.77E-02	2.60E-01	3.00E+03
ACETAMIDE	1.60E-07	1.85E-03	1.09E-04	1.26E+00	1.09E-04	1.26E+00

**Controversial, to be further investigated and confirmed in the next phase.*

Table 10 shows the atmospheric emission results when DEA is allowed to participate in the capture process.

Table 10 Emissions of MEA and its degradation products with DEA reactions (for simulated PCC for NGCC power plant)

Chemical Emissions	**As vapour**		**As droplets**		**Total**	
	mg/Nm^3 dry CO$_2$ lean flue gas	**mg/tonne CO$_2$ captured**	**mg/Nm^3 dry CO$_2$ lean flue**	**mg/tonne CO$_2$ captured**	**mg/Nm^3 CO$_2$ lean flue gas**	**mg/tonne CO$_2$ captured**
MEA	3.14E+00	3.62E+04	2.40E+00	2.76E+04	5.54E+00	6.38E+04
Ammonia	6.86E-04	7.91E+00	5.90E-03	6.81E+01	6.59E-03	7.60E+01
HEEDA	4.25E-15	4.90E-11	1.72E-09	1.99E-05	1.72E-09	1.99E-05
OXA	1.13E-10	1.30E-06	4.39E-07	5.06E-03	4.39E-07	5.06E-03
HEIA	1.95E-13	2.25E-09	2.54E-11	2.93E-07	2.56E-11	2.95E-07
TRIMER	6.32E-20	7.29E-16	2.84E-11	3.27E-07	2.84E-11	3.27E-07
CYCLIC UREA	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
POLYMER	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
DEA	1.01E-11	1.16E-07	6.57E-05	7.58E-01	6.57E-05	7.58E-01
FORMALDEHYDE	3.14E-01	3.62E+03	6.53E-06	7.53E-02	3.14E-01	3.62E+03
ACETALDEHYDE	3.26E-01	3.76E+03	3.90E-06	4.50E-02	3.26E-01	3.76E+03
ACETONE*	4.22E-01	4.87E+03	1.53E-05	1.76E-01	4.22E-01	4.87E+03
METHYLAMINE	2.60E-01	3.00E+03	7.61E-06	8.77E-02	2.60E-01	3.00E+03
ACETAMIDE	1.61E-07	1.86E-03	1.10E-04	1.26E+00	1.10E-04	1.26E+00

** Controversial, to be further investigated.*

On the basis of simulation results, it appears that the ranges of emissions of MEA and its degradation products from a capture unit linked to NGCC power plant will be as given in Table 11. It is to be noted that these values refer to the emission levels at the end of 3rd week when the reclamation of the solvent is usually recommended to reduce the concentration of degradation products accumulation in the circulating solution.

Table 11 Emission ranges of MEA and its degradation products per tonne of CO_2 captured (NGCC power plant)

Chemical Emissions	Minimum		Maximum	
	mg/tonne CO_2 captured	mg/Nm^3 dry CO_2 lean flue gas	mg/tonne CO_2 captured	mg/Nm^3 dry CO_2 lean flue gas
MEA	63400	5.4	63800	5.5
Ammonia	76.0	0.007	144.7	0.013
DEA	0.76	0.00007	2930	0.254
FORMALDEHYDE	3620	0.314	3620	0.314
ACETALDEHYDE	3760	0.326	3760	0.326
ACETONE**	4870	0.422	4870	0.422
METHYLAMINE	3000	0.26	3000	0.26
ACETAMIDE	1.26	0.0001	1.26	0.0001

** Calculations based on CO_2 density of 2.91 kg/m^3 at 175 kPa and 40 °C.*
*** Controversial, to be further investigated and confirmed in the next phase.*

There is a sizeable difference in the MEA emissions from the CFUS power plant and from the NGCC (Cf Table 7 and Table 11). The main difference is in the cooling step which is employed in the CFUS plant. The condensate thus produced will readily absorb the MEA and effectively remove it from the gas stream. This cooling step is not present in the NGCC but previous emissions modelling work showed that cooling the exhaust gas to low temperatures would result in effective removal from MEA from the exhaust gas in this case. This was not explored here as it was decided to confine the study to the study cases as defined in the IEAGHG report[1].

2.2.3 Nitrosamine Emissions

It is likely that the interactions between secondary/tertiary amines and NO_x components can produce nitrosamines. The latter has long been associated with health risks when the relevant concentrations exceeded levels determined by studies of health and environmental impacts. It is unlikely that there is nitrosamines formation from the direct degradation of the primary amine MEA. However, it is likely that selected secondary amine products resulting from the MEA degradation may produce nitrosamines. This aspect is the subject of ongoing research. Recently, Fostas et al[14] have reported formation of 23—6515 ng/g of N-nitrosodiethanolamine (NDELA), <1-4 ng/g of nitrosodimethylamine (NDMA) and 641.1 µg/g of diethanolamine (DEA) . Pedersen et al[39] have investigated degradation of MEA to form nitrosamines in their Aminox rig as well as in a high-pressure autoclave. Their experiments involved exposing 30 to 40 w% MEA solution to a simulated flue gas (containing 3.5 vol% CO_2, up to 14 vol% O_2 and 100 ppmv NO_X) at 44°C (absorber operating temperature) and 120°C (stripper operating condition). These investigators observed that NO is oxidised to NO_2 in the absorber inlet and roughly 20% of NO_2 is absorbed into the liquid phase. Their results indicate that ammonia is the primary degradation product of MEA and its production is strongly correlated with NO_X concentration in the flue gas. Whilst these investigators expected MEA being a primary amine not to form stable nitrosamine, they however detected 0.5 ppm (by weight) N-nitrosodiethanolamine (NDELA) under the absorber environment after 100 hours of solution exposure to NO_X (25 to 50 ppmv). Pedersen et al[39] believed that

NDELA may have been formed from diethanolamine (DEA) – a secondary amine - that may have been present in MEA solution as an impurity or a result of NO_X induced degradation of MEA.

Strazisar et al[40] reported to have observed the presence of nitrosamine compounds at the concentration of 2.91 µmol/ml of lean MEA solution in the 800 TPD post combustion CO_2 capture unit at Trona, California. This unit that has been built using Kerr McGee technology (approximately 15 to 20% w/w aqueous MEA solvent) has been in operation since the 1970's and treats a slipstream of flue gas from a coal-fired power plant. It is unclear from the publication for how long the lean MEA solvent had been in service prior to analysis; hence the extent of solvent degradation could not be determined. Also the level of purity or composition of the fresh solvent used was not reported hence the level of secondary amine contamination could not be determined. As the previously reported nitrosamines concentration found to be the only publicly available value from an operational unit that was reported in a refereed journal, it was important for us not to ignore its existence. While we acknowledge that the given number may not be representative for the reasons stated above we have used it as an example to show a possible extreme limit of nitrosamine production in the system.

For the purpose of calculating nitrosamine concentration, the ASPEN process modules were adjusted to include dimethyl-nitrosamine ($C_2H_6N_2O$) from the ASPEN library in the process stream composition. No attempt was made to include other nitroso compounds due to lack of relevant information which is required for simulation performed on ASPEN. This was a limitation of the ASPEN software and approach to this study but reflects the current state of knowledge.

Table 12 Calculated emissions of the modelled dimethyl nitrosamine ($C_2H_6N_2O$) using the loading of 2.91 µmol/ml of lean MEA solution as reported by Strazisar et al[40] (2003) (mg/tonne of CO_2 captured at the outlet of wash tower)

Nitrosamine Emissions	**As vapour**		**As droplets**		**Total**	
	mg/Nm^3 dry CO_2 lean flue gas	**mg/tonne CO_2 captured**	**mg/Nm^3 dry CO_2 lean flue gas**	**mg/tonne CO_2 captured**	**mg/Nm^3 dry CO_2 lean flue gas**	**mg/tonne CO_2 captured**
CFUS Power Plant	1.95E+00	6.12E+03	2.75E-02	8.62E+01	1.98E+00	6.21E+03
NGCC Power Plant	5.88E+00	6.78E+04	5.94E-02	6.83E+02	5.94E+00	6.85E+04

It should, however, be noted that there is no experimental or theoretical evidence that this particular nitrosamine (dimethyl-nitrosamine) will be present in a PCC process. Nevertheless, for the purpose of simulating emission of nitrosamine (in general) on ASPEN, this nitrosamine was considered in the lean MEA solution and its vapour phase. As a starting point, vapour phase calculations were carried out for CFUS as well as NGCC power plants at the concentration of 2.91 µmol/ml of lean MEA solution. The emission of this nitrosamine in the form of fine droplets was then calculated on the basis of assumed 0.13 m^3 liquid carry-over per million m^3 of gas stream.

Table 12 shows emission of dimethyl nitrosamine ($C_2H_6N_2O$) as a representative of all possible types of nitrosamine compounds formed at the outlet of the wash tower in a capture unit linked to CFUS and NGCC power plants. These conservative emission results represent the possible extent of degradation at the end of 3rd week of operation. It is recommended that these results showing excessively high concentrations should be viewed as qualitative numbers only because the concentration and type of N-nitroso compounds, if formed during the capture process, will be largely dependent on the operating conditions, type of flue gas and impurities.

However, in a recent publication Fostas et al[14] have reported formation of 23—6515 ng of N-nitrosodiethanollamine (NDELA)/g of MEA, <1-4 ng of nitrosodimethylamine (NDMA)/g of MEA and 641.1 µg of diethanolamine (DEA)/g of MEA. It is difficult to estimate the concentration of these compounds on per gram of CO_2 basis for Fostas et al's results as MEA to CO_2 ratio was not obvious in the paper. However, as an approximate estimate roughly 0.5 mole (22 g) of CO_2 is absorbed by a mole (61 g) of MEA. Therefore in the MEA solution a maximum concentration of about 18046 (61*6515/22) ng of NDELA/g CO_2, 11.8 (61*4/22) ng of NDMA/g CO_2, 1776 (61*641/22) µg of DEA/g CO_2 may be present in the MEA solution. The exact concentration of these degradation products in gaseous CO_2 will depend on the phase equilibrium conditions. Under a worst case scenario if most of these degradation products are volatilised with CO_2 then their concentration in gas phase will be closer to what is approximately estimated per g of CO_2 in the liquid phase. Considering this argument the estimated highest possible levels of nitrosamine emission by our simulation seem to be well within the range published by Fostas et al[14].

3 PROCESSES FOR PCC UNIT EMISSION CONTROL

As described in the earlier chapter, the exit gas streams of CO_2-lean flue gas and carbon dioxide product from the PCC unit could have amine and its degradation products in fine droplet as well as vapour form. Therefore droplet and vapour separation processes are required to capture all emissions from the PCC unit. Since chemicals present in the liquid phase and their interactions are precursors of all gaseous emissions, a preventive approach will be to minimise the levels of degradation products in the liquid phase. This approach will also reduce the concentration of the degradation products in the fine droplets. However, this study mainly deals with the processes and equipment for removal of emissions in the exit gas streams and very briefly highlights the significance of removal of amine degradation products in minimising gaseous emission, which could be considered in future work.

Considering separation of gases and fine droplets of liquid from exit streams, scrubbing, cooling, adsorption and mist elimination processes, which are fairly mature in industry, seem to be the suitable approach for the control of PCC related emissions. According to the literature reviewed, there is limited information as to the control of emissions from PCC processes as this is a fairly new area of activity in industry.

A summary of published methods, their limitations and further need for research to adopt them for amine process is presented.

3.1 Scrubbing to capture vapours

Scrubbers are well known in the process industry for extracting condensable or soluble vapour from gases. MEA vapours and its degradation products are conventionally captured by water wash or a scrubbing stage or several stages with de-mineralized water[41], acidic water[42] and with special reagents[43].

3.1.1 Single and multiple stage water wash

The water washing section in the conventional absorber column is a one stage process (Figure 10), in which the concentration of amine recovered in the washing water is so high that the recovery of amine is insufficient due to poor partitioning of amine between the gas phase and the highly concentrated solution in washing water. In this situation a large amount of amine vapour remains unextracted by the wash water and is carried away with the CO_2-lean exhaust gas and released outside of the de-carbonation system, perhaps to the surrounding atmosphere.

A multiple stage water washing method has been developed to address amine emission due to the saturation of wash water[41] as referred to above. This method as described in the literature[41] involves modification of the absorption column to include three stages of water washing to absorb amine from the combustion exhaust gas (Figure 11). However, the optimum number of washing stages would actually depend on the operating conditions and have to be determined to achieve a cost effective control of emission. It is to be noted that lower concentrations of amine vapour in the CO_2-lean gas stream will require larger numbers of theoretical stages of extraction into wash water. This essentially means more trays at additional cost. The literature does not provide any information about an optimum number of stages that will be required to minimise the emission. It seems that the optimum number of washing stages will largely depend of the level of acceptable emissions at the installation site and have to be determined in co ordination with the local environmental authorities.

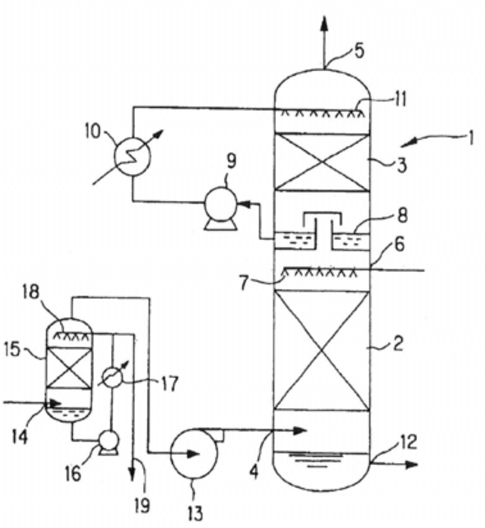


Figure 10 Flow scheme of conventional amine based CO_2-capture with single stage washing on the top of absorber column[41] (1 absorption tower, 2 carbon dioxide absorption section, 3 water washing section, 4 exhaust gas supply section, 5, 6, absorbing solution supply port, 7 nozzle, 8 liquid reservoir in a water washing section, 9 circulating pump, 10 cooler, 11 nozzle, 12 absorbing solution discharge port, 13 blower, 14 exhaust gas supply port , 15 exhaust gas cooler, 16 circulating pump, 17 cooler, nozzle, 19 drainage line)

The multiple wash provides (a) effective recovery in more than one stage of counter current contacting of cold water with CO_2-lean exhaust gas (b) recycling of regeneration tower refluxed water as washing water and enhances the washing with large quantity of water to ensure lower concentration of amine in wash water and therefore low evaporative losses of amine, and (c) withdrawal of washing water from the water washing section in the succeeding stage (top) and supplied to the water washing in the preceding stage (lower) to enhance the amine recovery by maintaining low concentration of amine in the succeeding stage.

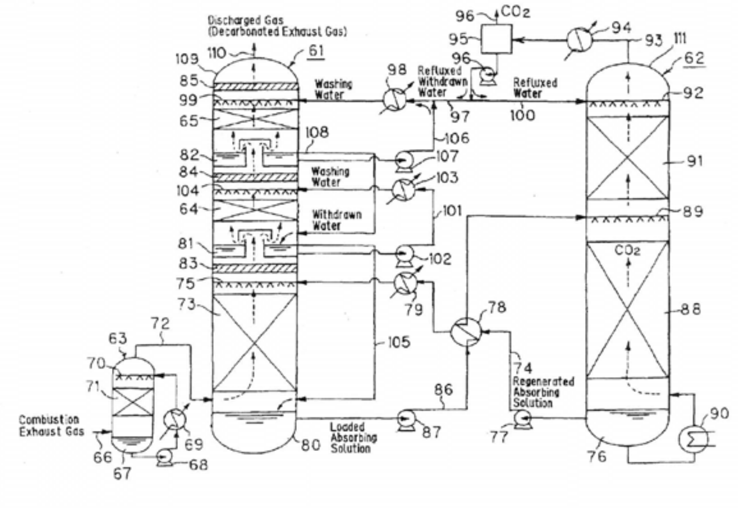


Figure 11 A flow scheme showing three stages of washing on the top of absorber column[41]
(61 absorption tower, 62 regeneration tower, 63 cooling tower, 64 first stage of water washing section, 65 second stage of water washing section, 66 exhaust gas supply line, 67 bottom of cooling tower, 68 circulating pump, 69 heat exchanger, 70 nozzle, 71 charging section, 72 exhaust gas supply line, 73 CO_2 absorption section, 75 outlet nozzle at CO_2 absorption section, 76 bottom of regenerator tower, 77 absorbing solution supply pump, 78-79 heat exchangers to cool regenerated absorbing solution, 80 bottom of the absorption tower, 81 liquid reservoir, 82 liquid reservoir, 83-84-85 demisters, 86 absorbing solution discharge line, 87 absorbing solution discharge pump, 88 Lower section of regenerator tower, 89 nozzle, 90 reboiler, 91 upper discharging section, 92 nozzle, 93 carbon dioxide discharge line, 94 condenser, 95 CO_2 separator, 96 CO_2 release line, 97 regenerator tower refluxed water supply line, 98 heat exchanger, 99 nozzle, 100 reflux line, 101 circulation line, 102 circulation pump, 103 heat exchanger, 104 nozzle, 105 reserved water discharge line, 106 recirculation line, 107 circulation pump, 108 reserved water discharge line, 109 top of absorption tower, 110 gas release, 111 top of regenerator.)

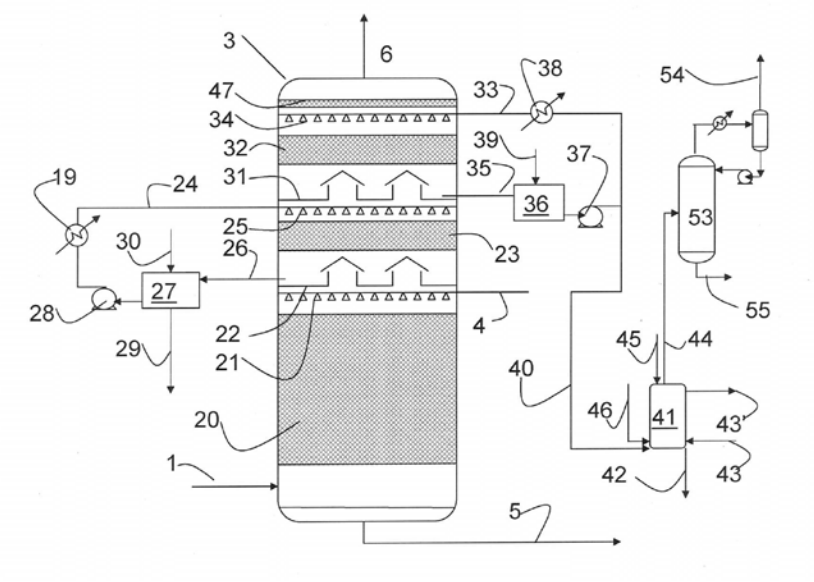


Figure 12 Modified absorption column with acid wash[44]
(6 de-carbonised gas exit, 19 external cooler, 20 absorber contact zone, 21 liquid distributor, 22 collector plate, 23 washing zone, 24 washing water line, 25 water distributor, 26 water line, 27 water wash tank, 28 pump, 29 water bleed line, 30 water makeup line, 31 collector plate, 32 acid washing zone, 33 acid wash line, 34 distributor, 35 liquid collector line to acid wash tank, 36 acid wash tank, 37 pump, 38 optional heart exchanger (heater or cooler), 39 acid makeup line, acid wash bleed line, 41 amine reclaimer, 42 non-volatile and solid waste discharge, 43 condensing steam, 44 reclaimed steam and amine exit, 45 alkaline solution feed line, 46 line to run reclaimer in batch mode 47 demister, 53 fractionation column, 54 ammonia disposal line 55 amine and water exit to the main solvent loop.)

The concentration of amine in the exhaust of the CO_2-lean flue gas could be brought down from 25 ppm for single washing stage to around 8 ppm for three washing stages[41,45,46]. In the three washing stage when the liquid withdrawn from the second-stage water washing section (washing water) was not supplied to the first-stage water washing section, the amine concentration in the exhaust of de-carbonised gas was reported to be 11 ppm[41,45,46]. Several wash sections in the absorption column (Figure 11) could make significant reduction in the emissions from the absorption column[41,45,46], however this approach has certain limitations:

(a) The concentration of amine in the wash water has to be kept low to prevent excessive formation of amine vapour which could generate excessive pressure and interrupt the flow of wash water in the recirculation loop as a relatively higher pressure in wash section will not allow flow of wash water at relatively lower pressure,
(b) High vapour pressure of amine may give high amine emission to atmosphere,
(c) Lowering temperature of wash water can reduce the amine vapour pressure but excess dilution may increase the equipment size, water consumption, energy required for wash water pumping, and energy for cooling the wash water,
(d) Cooling and dilution may not be effective as gaseous impurities may not be soluble in water and their critical temperature is also well above the wash water temperature. Cooling also reduces buoyancy of the exhaust gases.

3.1.2 Combined acid and water wash

The acid wash technique patented by Aker Clean Carbon[42] involves protonation and stabilization of amines and other alkaline degradation products in the solution. This substantially reduces the concentration of amine including ammonia in the liquid phase and hence in the vapour phase. The important part of the invention is the modified absorber column (Figure 12), which has three contacting zones divided by two collector plates with the bottom one for contacting between the flue gas and amine solution. In the middle zone the upward moving flue gas is contacted with a counter current flow of water. The wash water is (1) recycled to minimize the water consumption and control the amine concentration in the wash water, (2) cooled to keep the vapour pressure of amine low, and (3) partially bled to prevent build up of high concentration of amine and other degradation products.

The washed flue gas then moves upward into the top zone where it is washed with acidic aqueous solution. The pH of acid aqueous solution is preferably kept between 4 and 6, but also works between 3 and 7. The acid aqueous solution is recycled through the washing zone to keep a relatively higher concentration of amine salt and a bleed, either continuously or in batch, is sent to a reclaimer to recover amines.

The reclaimer is a boiler where amine solution is boiled to release steam and amine which are then transferred to the lower part of the amine solution regenerator column. In order to reduce the cost and complexity of the unit usually a single reclaimer unit is installed to reclaim amine from the water washing solution bleed as well as a bleed from the main absorbent that is withdrawn from the regenerator. An alkaline solution, usually soda ash or sodium hydroxide, is injected to dissolve the salts and recover the amines in the reclaimer. The reclaimer could be an ion exchange or dialysis system besides being a thermal type. Acids could be either inorganic or organic such as sulphuric acid, phosphoric acid, nitric acid, acetic acid, formic acid, carbonic acid, citric acid etc., as recommended in the literature[42].

As claimed in the patent[42], with the conventional unit about 90% of CO_2 was captured from a gas turbine exhaust by 30 w% MEA solution passed through the absorber. The 90-100 ppm of gaseous MEA with the flue gas at 55-57^{o}C was present in the exhaust from the absorber section. With single stage water washing using cooled water, the MEA concentration in the flue gas was reduced down to 0.7 ppm. Ammonia concentration was reported[42] to be about 30 ppm (wet) measured by FTIR and about 0.4 µg/Nm^3 of N-Nitrosomorpholine was detected in the flue gas. In the patent the details of operating conditions such as size of the PCC unit, temperature, flow rate of flue gas and MEA solution and the composition of flue gas, etc. are not presented and this data about N-Nitrosomorpholine need to be further confirmed. However, regarding other nitrosamines Fostas et al have recently reported[14] formation of 23—6515 ng of N-nitrosodiethanolamine (NDELA)/g of MEA, <1-4 ng of nitrosodimethylamine (NDMA)/g of MEA and 641.1 µg of diethanolamine (DEA)/g of MEA.

3.1.3.1 Sulphuric acid for acid wash

When sulphuric acid was add to reduce the pH of recycling water below 6, the MEA concentration in flue gas was dropped below detection limits which was reported[42] to be around 0.05 ppm. Ammonia concentration decreased below 1 ppm and no N-Nitrosomorpholine was detected in the emitted flue gas[42].

3.1.3.2 Carbonic acid for acid wash

Dissolved CO_2 is acidic and CO_2 absorption in the wash water reduces the amine vapour pressure to some extent[42]. Dissolved CO_2 forms carbonic acid and could enhance the solubility of amine in wash water as amine forms carbamates with CO_2. However, the solubility of CO_2 in wash water is low due to the low partial pressure of CO_2 in the CO_2-lean (scrubbed) flue gas and therefore the concentration of CO_2 in wash water is not sufficient to absorb all amine and reduce its vapour pressure. Carbonic acid could be produced in situ by increasing the CO_2 pressure, by increasing the CO_2 concentration in the acid wash water system by injecting concentrated CO_2 in circulating liquid, by using water that has been contacted with CO_2 gas at high pressure, by addition of bicarbonate salts and/or lowering the temperature of wash water in contact with CO_2. The condensate from the stripper overhead condenser, or condensate from the CO_2 compressor intercoolers, are highly enriched in CO_2 and hence viable source for makeup solution wash system, where additional acid could be added to obtain a pH of the preferred range[42]. When carbonic acid is used the recovery of ammonia and amine could be performed without addition of alkali and by simply boiling off the liquid from acid wash then separating ammonia and CO_2 in a fractionating column. Since CO_2 does not form a stable chemical compound with amine, the acid wash using CO_2 could be considered as a weak chemisorption process.

3.1.4 Deep Removal of Nitrosamines

As referred to earlier there has been increasing focus on the possibility of emissions of carcinogenic nitrosamines produced during the PCC process. The acid wash technique is reported[42] to be effective in reducing the emission of nitrosamines.

3.1.5 Proprietary Reagents

Mitsubishi Heavy Industries (MHI) has also developed a zero amine emission system[47,43]. This system uses a special reagent in the water washing section to capture amine, degraded amine, ammonia, formaldehyde, acetaldehyde, carbonic acids and nitrosamines. With the zero amine emission technology as claimed in their presentation, there was no amine detected at the exhaust and the concentration of amine degradation products was less than 0.2 ppm as vapour.

3.1.6 Destructive method for Nitrosamines-UV, Plasma and Oxidation

Due to the toxicity[48,49,50,51,52,53]. of nitrosamines the destruction and/or removal of the compound in liquid or gas phase by advanced oxidation processes (AOP), photolytic methods, radiolytic destruction, chemical reduction and biodegeneration has also been reported[54]. It will be, however, important to know the products of nitrosamine destruction and how they affect overall emission and performance of the PCC process

N-nitrosodimethylamine (NDMA) molecules absorbs UV radiation in the wave length range of 225-250 nm with maximum absorption at 238 nm[55]. It has been observed[56,57,58] that an acidic pH enhances the absorption of UV radiation and favours destruction of nitrosamines whereas alkaline pH may retard the destruction process. This suggests irradiation of gaseous as well as liquid streams after acid wash stage in the absorber column will be effective in reducing emissions of nitrosamines. However, the effect of nitrosamine destruction products on the amine solvent requires further investigation as this might be dependent on the type of nitrosamines, composition of flue gas and operating conditions. According to the literature mainly parent amines were observed to be the main by-products of the photolysis[59].

Besides UV methods, there are several other methods reported for the destruction of nitrosamines. Electron pulse radiolysis could be effective in destroying higher nitrosamines[60] but not so effective in destroying NDMA[61]. Ozonation alone was reported to be not very effective for the destruction of NDMA which was only 13% destroyed at neutral pH but O_3/H_2O_2 process was reported to be effective in removing up to 80% of NDMA within 5 minutes[62,63]. According to Lee et al[62] methylamine was reported as the main product of

NDMA destruction by O_3/H_2O_2 process which could be favourable for PCC processes. Plasma technology is also known for oxidative or thermal destruction of volatiles, however further research will be required to adopt this for PCC processes.

Both UV radiation and UV/O_3 processes are equally efficient in NDMA removal but the former mainly produces dimethyl amine and nitrate whereas the latter mainly produces nitrates[63]. This indicates that the latter may not be suitable for PCC process as the latter completely destroys NDMA to nitrates whereas the former partially turns it into recyclable amine.

According to Plumlee and Reinhard[64] solar photolytic destruction of NDMA is more efficient than biodegradation, even at low levels of radiance. A number of bacteria and enzymes have been identified for biodegradation of NDMA but they all require long residence time and the by-products are methylamine, nitric oxide, nitrate, nitrite and formate. Plumlee and Reinhard[64] have reported an average of about 42% degradation of NDMA present in tertiary waste water treatment plant (WWTP) effluent which was passed through solar channels with a residence time of about 83 minutes. The half lives of NDMA for London's latitude were 8-38 hours[64,65]. According to Chen et al, solar photolysis is the cause for the degradation[66]. Biodegradation methods were reported as slower than photolytic degradation and therefore likely to require longer residence time[64]. There is no report found on rates of degradation or residence time required by ozonolysis. Further research is required to assess suitability of biodegradation for the treatment nitrosamine in a PCC unit[54].

Nickel plated iron has been found to reduce NDMA to DMA and ammonia[67,68,69], but this process requires hydrogen and certain pressure therefore may not be quite suitable for a PCC unit.

At this stage of development in this area it is not possible to judge which technology will be ideally suitable for the PCC unit and some additional review and laboratory trials will be required to evaluate the suitability of these approaches.

3.2 Adsorption to capture vapors

Adsorption could be used to capture and recover all gases and vapours. There is no reference in the literature related to capture of amine and its degradation products, however removal of polar as well as non-polar volatile organic compounds has been subject of research for nearly three decades and some of these technologies are commercially available[70,71,72].

These technologies with the existing adsorbents or new adsorbents, which could be specifically designed for amine compounds, could be extended to capture the emissions from the MEA unit. A relatively small PSA unit with shorter cycle time could be designed with specially designed adsorbents. The greatest advantage of adsorption processes are their low energy requirements, practically no moving parts, no chemical or water usage. The process also provides flexibility in terms of choice of adsorbent, size of adsorber vessels and selection of time cycle. With these flexibilities a pressure swing adsorption (PSA) unit could be designed for any given level emissions to be captured and the extent of separation required. However, the cost of the unit significantly depends on the level of emission and extent of separation required. In principal almost 99% separation of MEA, ammonia and other degradation product could be possible; however the separation over 90% usually becomes economically unattractive. A schematic flow diagram of a typical regenerative adsorption separation system[55] is shown in Figure 13. The preferred regeneration mode should be vacuum swing at ambient temperature as this has negligible energy losses compared to temperature swing. Some energy is required for operating a vacuum pump but almost all amine and amine products could be recovered. However, additional work is required in identifying and developing specific adsorbents.

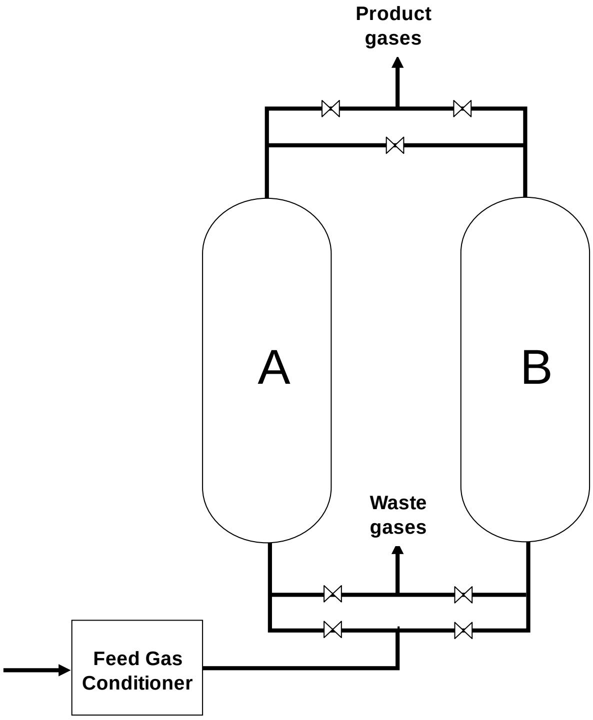


Figure 13 Flow scheme of typical pressure swing adsorption unit for removing impurities from gas[73] *(A and B are absorbers)*

A non-regenerative adsorption system with acid treated activated carbon as adsorbent could be used to capture amine and amine degradation products. However, the cost of non-regenerative sorbent could be significantly high. Moreover, the amine recovery and disposal of spent adsorbent could be an issue which requires further work.

Since CO_2-lean gas is saturated with water the adsorbers for the PSA unit will have to be provided with appropriate regenerable dehumidification zone to prevent water poisoning of the adsorbents for gases. If more gaseous products have to be separated a multi zoned adsorber with different adsorbents may have to be optimized for this separation.

It is known that the PSA technology will require a compressor to raise the pressure of gas and this will add to the capital and operating costs. This may be true and a vacuum swing adsorption (VSA) may prove to be more suitable as it does not require a compressor. However, it should also be noted that the VSA technology requires a vacuum pump along with a surge vessel to regenerate the adsorbers. Moreover, a VSA unit requires three adsorbers as compared to two adsorbers in a PSA system for continuous operation. In addition to that the adsorber size in the case of VSA is several times larger than in the case of PSA due to significantly higher adsorption capacity of the adsorbents at higher pressures. A detailed study will be required to assess whether, PSA, VSA or PVSA (Pressure and Vacuum Swing Adsorption) will be suitable for this process.

3.3 Cooling or condensation to separate vapors

Freeze drying and cryogenic separation is also well known for separating trace impurities and moisture from gases. For example, hydrogen gas drying and purification for turbogenerator cooling to maintain its rated efficiency is very well known[74,75,73]. In the freeze drying process the gas is usually cooled down to a temperature in the range of 5 to 10 ^{o}C to condense all vapours which have their dew points above this temperature range. The freeze drying system involves a pre-cooler for the gas which exchanges heat with the gas stream already cooled in a condenser as shown in Figure 14. The condensate is intermittently drained from the condenser. The freeze drying method will be suitable for a number of degradation products which may have dew point above 5 ^{o}C. It may also effectively separate some of the water soluble vapours which may get dissolved in the condensed water.

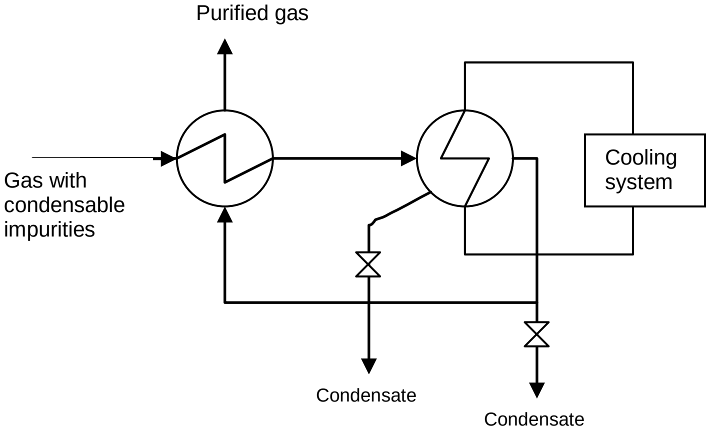


Figure 14 Schematic flow diagram of a freeze drying system

The cooling of gas streams to temperatures below the dew point of the gas components present in the mixture will result in the condensation of these components, which can be subsequently removed in droplet separator. As flue gases contain water vapour, and most of the acid gases have been removed in a PCC process, water will be the main product. It has been shown in the process simulation results (Section 2.2) that the condensate will also readily absorb water soluble gases and vapours from the flue gas. As such gas cooling is an excellent way to remove water soluble components from flue gases. However, to obtain deep removal it is required to go to sub-zero temperatures where the formation of ice rather than liquid water forms an added complexity.

3.4 Demisters to remove fine droplets of liquid

The conventional method of capturing entrained fine droplets of liquid involves use of demisters or mist eliminators. All demisters work on the principle of capturing fine droplets entrained in a gas phase in such as way that they are not re-entrainable into the gas phase. As shown in Figure 15, the mechanism could be: (1) by changing the direction of the gas stream thereby inducing inertial impaction of the heavier droplet or by reducing the velocity of the droplets below their terminal settling velocity and intercepting them with static surface, (2) by allowing the fine droplets (<5 µm) to diffuse through very narrow spaces smaller than their mean free path and then impinging on a surface due to Brownian motion (3) by directly impinging onto a surface.

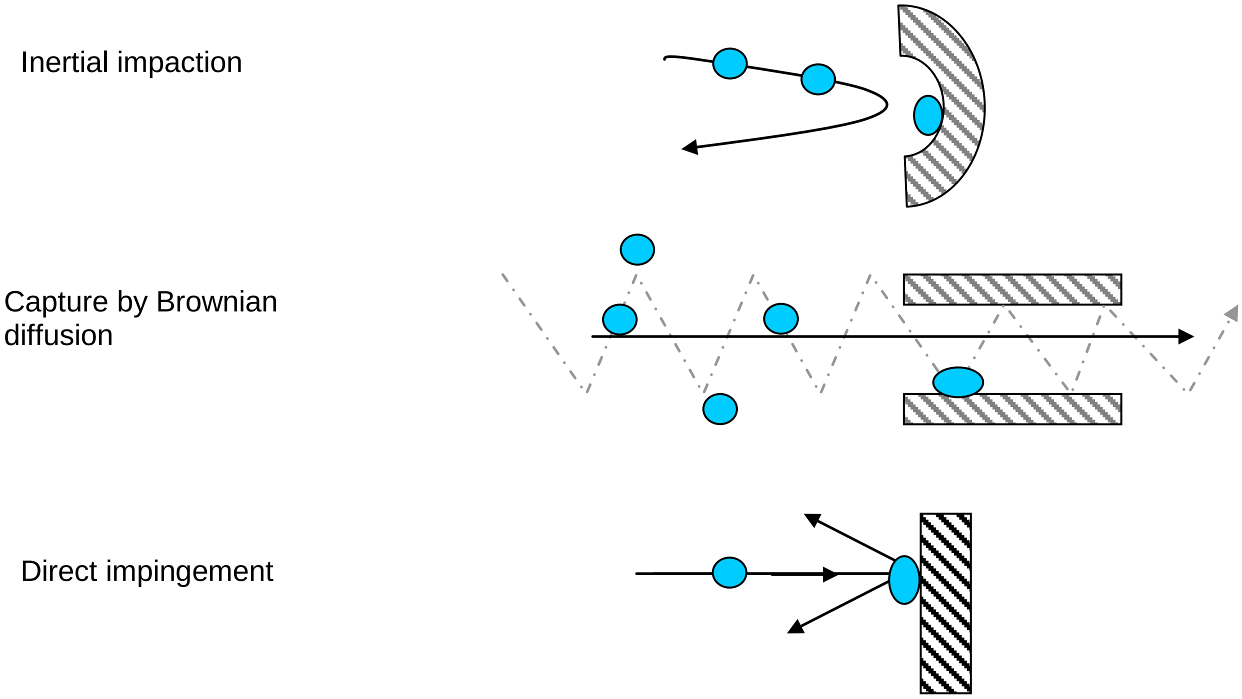


Figure 15 Mechanisms of operation of demister

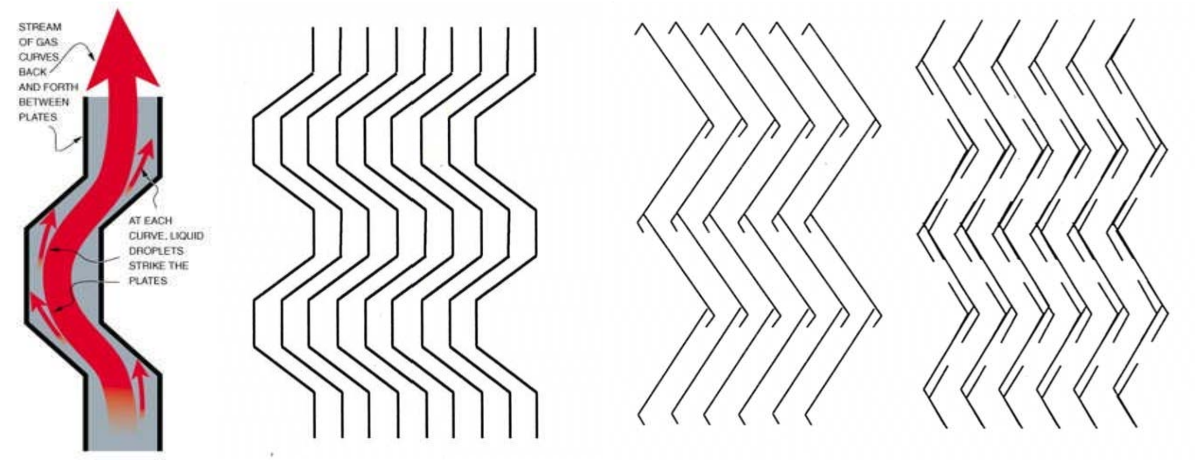
The demisters are quite efficient and most of those which operate on the principle of direct impact and interception or terminal settling velocity could achieve up to 100% separation of droplets above 5 µm. In order to achieve very high efficiency of separation in submicron range special fibres are embedded into the mesh of the demister to arrest the droplets through Brownian diffusion.

There are several types of demisters commercially available. Some of the commonly used ones are Vane demister, Wire mesh demister, Swirl demister, Multicyclones etc.

3.4.1 Vane demisters

A vane demister operates on the principle of direct impact. As shown in Figure 16, it consists of a series of parallel plates or vanes spaced at specified pitch to provide passage between the plates for gas to flow, The plates are profiled (“W” or “VH”) with angles to provide sufficient change of direction for liquid droplets to impact, coalesce and drain from the surfaces of the plates (Figure 16a).

Depending on the profile of the plate, the vane demister could be W, VH-1 or VH-2 type as shown in Figure 16. In W type vane the droplets impinge and coalesce on the vanes as gas flow is around the vane profile. This vane type suits vertically upward flowing gas with high liquid load. The VH type vanes are very efficient and are suitable for horizontal flows as H profiles provide pockets for liquid collection.



(a) (b) (c) (d)

Figure 16 Vane type demister manufactured under tradename AlphaMIST by HAT International *(a) mechanism of separation by direct impact of droplets on plates, (b) W or V V type demister for vertical flow (c) VH-1 type demister for horizontal flow, (d) VH-2 demister for horizontal flow.*

The performance of AlphaMist W, VH-1 and and VH-2 demister is shown in Figure 17, which indicates that these demisters are most effective under gas velocity corresponding to the K factor of 0.15 m/s. The K factor is a proprietary design parameter of the manufacturer and is defined in the Souder-Brown equation as:

$$V_{\max} = K\left(\frac{(\rho_L - \rho_V)}{\rho_V}\right)^{0..5} \qquad (17)$$

Where, $V_{\max}$ is maximum velocity in vane, ρ_L, ρ_V are liquid droplets density and vapour density respectively. K factor is also called vapour load factor, system load factor or Souder-Brown velocity a measure of relative velocity of liquid droplet in gas at given pressure. If the K value is kept constant for two different pressures then the liquid droplet velocity with respect to vapour will be same for the two pressures.

Amongst AlphaMIST vane demisters, the VH-2 is the most effective demister for fine droplets.

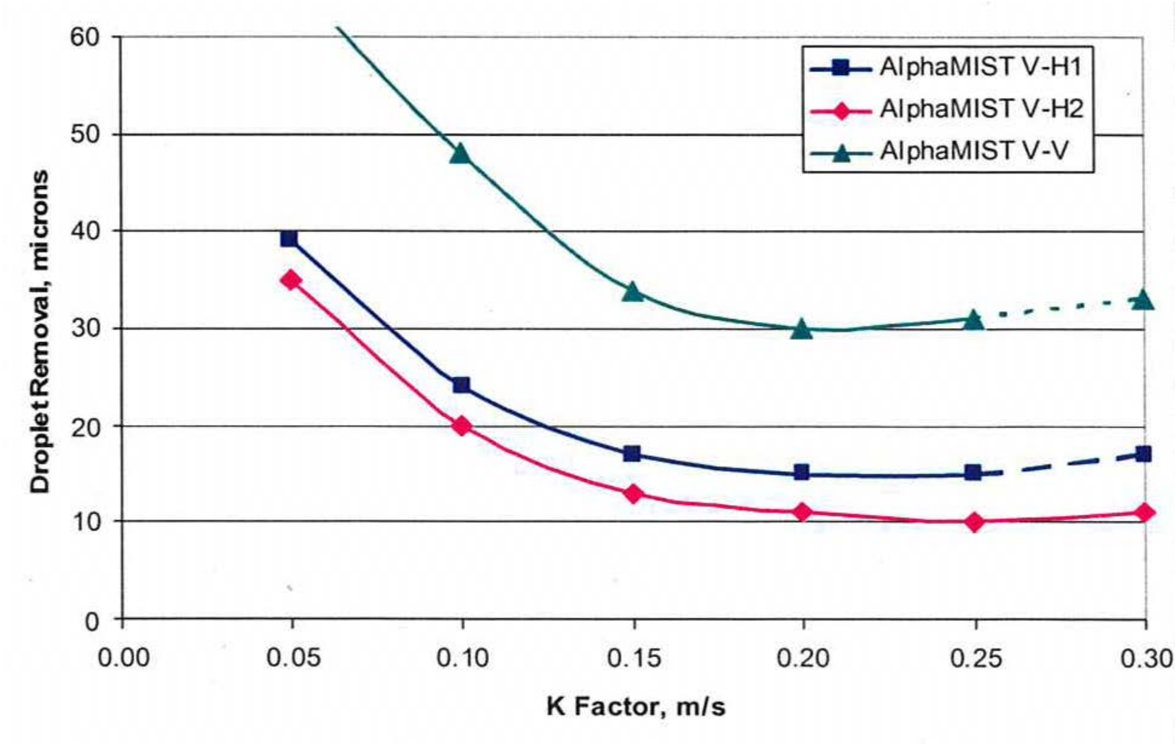


Figure 17 Performance of Vane type demisters

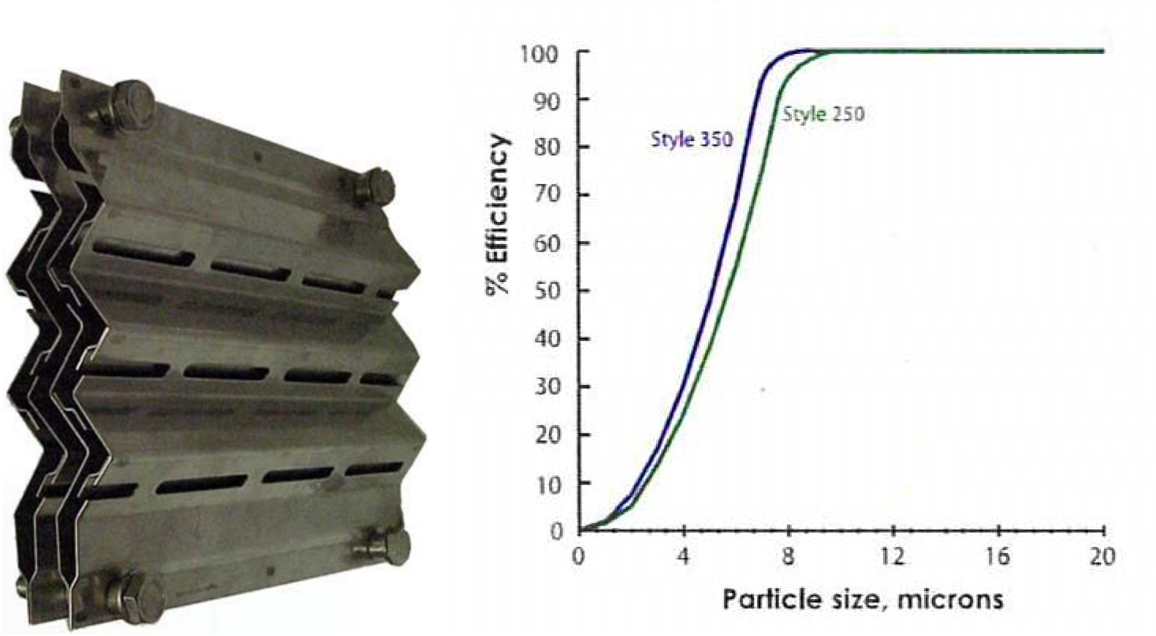


Figure 18 Picture of 350 style demister for vertical upward flow on the left side and performance of 350 and 250 style Flexichevron demisters on the right side

Flexichevron mist eliminators (manufactured by Koch-Otto York Separation Technology) are similar to AlphaMIST VH-2 type vane demisters and they can have almost 100% efficiency for droplets size between 8 to 40 µm. Figure 18 shows the picture and performance 250 and 350 style of Flexichevron demisters which are designed for vertical upwards and horizontal flow, respectively.

3.4.2 Wire mesh demisters

The wire mesh demister (Figure 19) is a compact pad of wire mesh through which gas is passed freely but liquid droplets having inertia cannot follow the gas path and come in contact with wire surface, where more droplets coalesce into large drops and fall due to gravity.

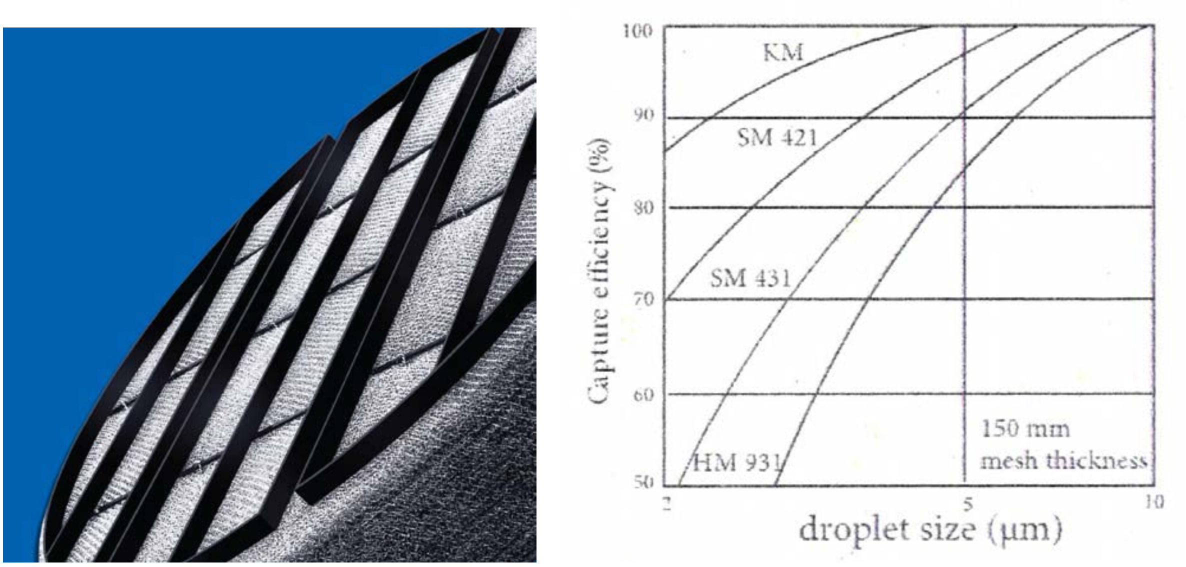


Figure 19 Picture of Mistscreen Mist Eliminator on the left side and performance of four types of Mistscreen of the right side.

A demister pad known as Misterscreen manufactured by Haever and Bocker, Germany, is fabricated from knitted wire of metallic or synthetic materials to suit various processes. It can achieve 99.9% separation efficiency for droplets >10 µm.

3.4.3 Swirl Mist Eliminators

The demister consists of special separating elements fixed on a tray with openings for draining liquid (Figure 20). Each separating element has an outer tube with integral swept inlet nozzle fitted with a special internal swirler. In the swirler the gas containing liquid droplets is accelerated at high speed into a cyclonic swirl thereby liquid droplets are flung to the tube wall and impinge on the wall. The coalesced drops are then swept forward with the gas and captured by a centrifugal separator cap on the top. The captured liquid then falls on to the tray deck outside the element tube. Swirl mist eliminators (SME) are designed specifically for a high efficiency (99.99% for droplets size <5 µm in Figure 21) of gas-liquid separation and high capacities. The high speed SME elements are available in a range of materials including low cost/weight glass reinforced plastics, stainless steels, and high wear resistant ceramics.

Figure 20 Swirl Mist Eliminator (SME) unit (left), swirler (middle), and SME fitted on tray (right)

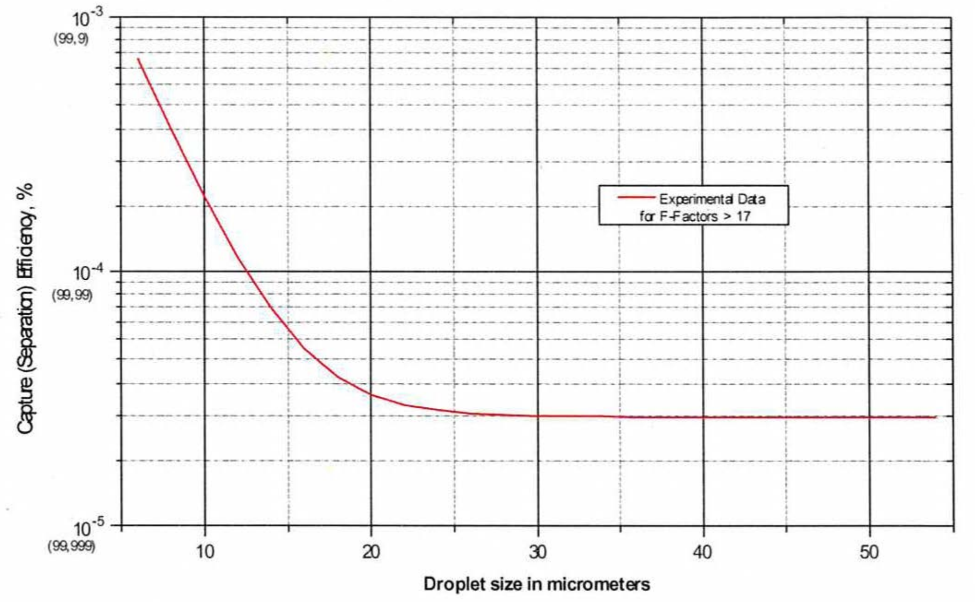


Figure 21 Performance of a SME unit

3.4.4 Multicyclones

Multicyclones could also be used instead of SME for separating droplets above 25 µm and for higher flows of gases with heavy loading of liquid (Figure 22).

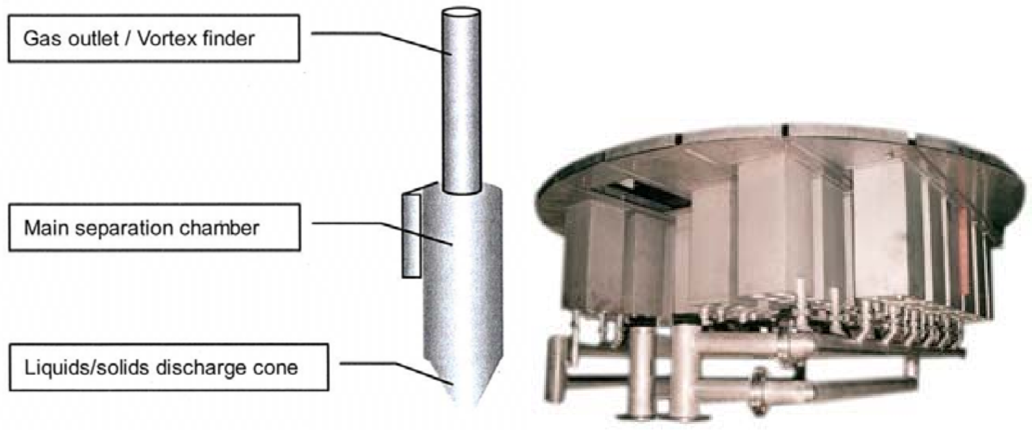


Figure 22 A single element of cyclone (left) and a multicyclone (right)

3.4.5 Brownian demisters

Brownian demister candles are also commercially available from Chemplast UK Ltd, and Amistco (Licensee of Begg Cousland). Candle filters remove liquid droplets by means of impaction if the droplets are larger than 3 µm, interception if the droplets are larger than 1-2 µm, and Brownian diffusion if the droplets are submicron (<1 µm). Each filter is composed of millions of fibers (Figure 23), resulting in very high collection efficiencies through their cumulative effect. Low approach velocities are necessary in order not to mask the diffusion velocities associated with Brownian movement. Candle filters are installed vertically and gases pass horizontally through the filter wall, the trapped droplets coalesce and drain through the filter bed. A comparison of Brownian diffusion type candle and impaction type candle is shown in Figure 24, which clearly indicates a significantly higher separation efficiency of the Brownian diffusion type candle.

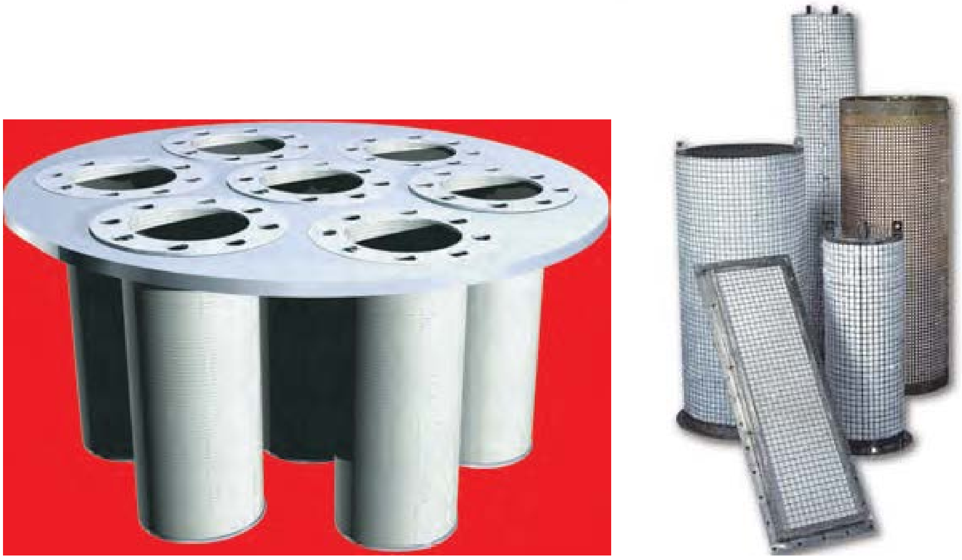


Figure 23 Brownian diffusion demister candles

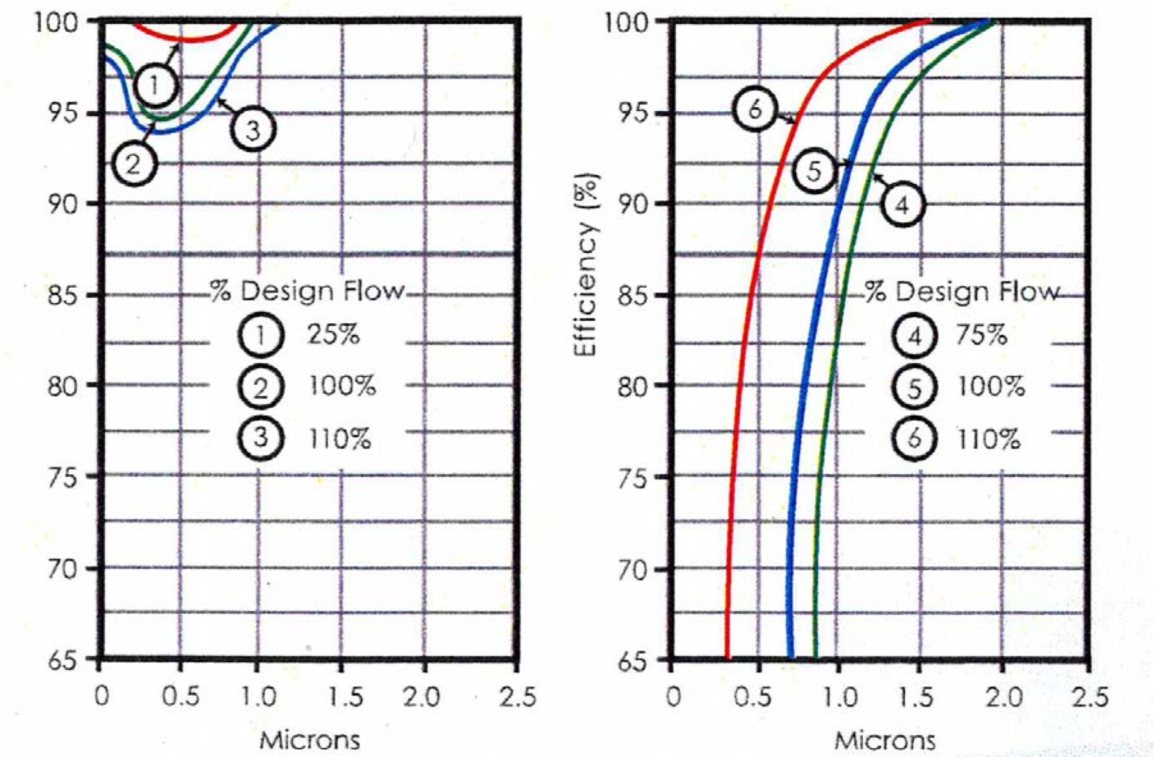


Figure 24 Performance of Flexifiber demister of Brownian diffusion type (left) and Impaction type (right) manufactured by Koch-Atto York Separation Technology

3.5 Evaluation of state-of-the-art methods for removing each species emitted

There are very limited number of reports on this topic in the literature reviewed[41, 43-44]. Consequently a number of parallels are drawn from the known methods[70,71,72,74,75,76] from other applications and then these methods have been applied to estimate the possible reduction in emissions from MEA based CO_2 capture units. There are also uncertainties about the type and rate of emissions possible from actual units as very limited data have been published.

Originally MEA based capture processes were developed for natural gas sweetening and the degradation of amines and the emissions from the amine process was not an issue[77]. However, the application of the process to flue gas from coal fired power stations has raised the issues of amine degradation and potentially harmful emissions. As a result research has began to elucidate degradation mechanisms[78].

A number of emissions have been identified in CO_2 capture units[79,37,38,35,80]. The estimated emissions of amine vapour at absorber feed gas temperature and stack gas temperature is shown in Figure 25.

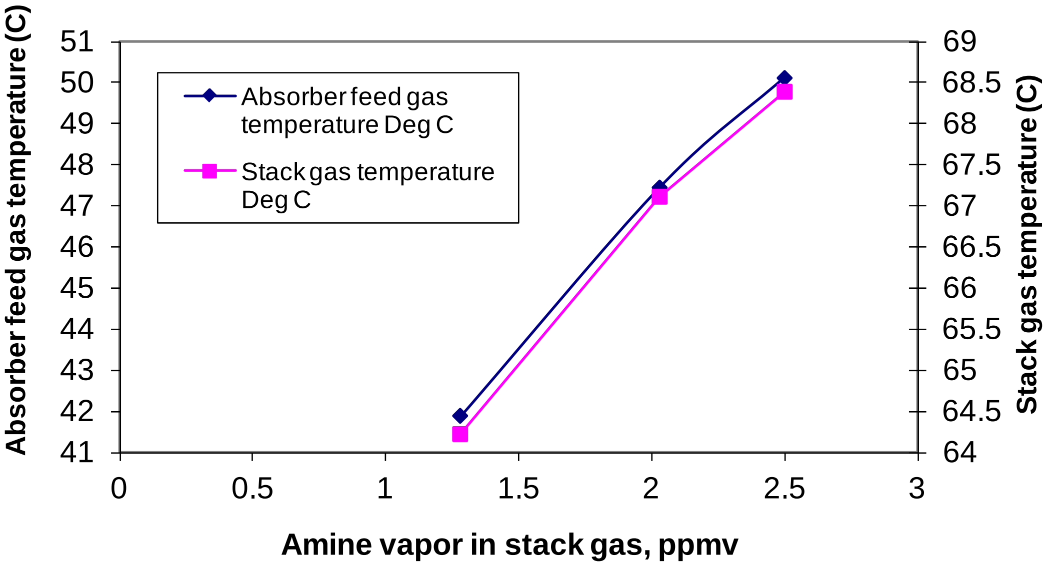


Figure 25 Variation in amine vapour loss with absorber feed gas temperature and stack gas temperature[79]

On the basis of simulation results described in the earlier section, the data available from the literature, the anticipated concentrations of various chemicals present in the gaseous emission are summarised in Table 13. The emission of fine droplets entrained in gas is described in Table 14.

As shown in Table 13, the most predominant emission is anticipated to be ammonia, MEA and various nitrosamines. Note that the nitrosamine emissions reported in Table 13 have been based on the reports by Bade et al[42], Mitch et al[55] and Xu et al[56] and may be significantly overstated. As previously described the emission rates have been used in the current work as they are the only publicly available data even though there are uncertainties as to their representativeness as there is no information as to how long the solvent may have been exposed to the flue gas. The formation of nitrosamine and other degradation products and their fate in the atmosphere should be experimentally evaluated in a laboratory scale reactor connected to a SMOG chamber test facility. Note also in Table 13 that the concentrations of all other species are at very low level. Considering boiling points of the anticipated emissions some of the carboxylic acids may expected to have considerable vapour pressure in the absorber but due to interaction with amine and ammonia in the solution these acids are likely to be neutralised and remain in solution.

As rated on Table 13, the most effective method for capturing amine would be acid wash as (1) it can capture most of the chemicals which are weak bases, and (2) acid wash could easily be incorporated in the new designs and could also be retrofitted. Washing with special agents which are proprietary products of some technology developers may be very effective but their performance data is not available. UV, O_3, O_3/H_2O_2' and plasma methods are quite effective in removing nitrosamines and perhaps also effective on ammonia and other photosensitive amines but such data is not available in the literature. However, a combination of acid wash followed by UV treatment seems to be ideal as UV treatment is effective in acidic pH.

Table 13 Anticipated effectiveness of the separation of amine and its anticipated degradation products from the CO_2-lean flue gas stream by various methods ([1] without acid wash, "-" data not available, "0" undetectable, "*" overstated values need to be experimentally verified)

Compound	Polarity/Boiling point range (°C)	Anticipated concentration range (ppmw)	Anticipated concentration after removal possible with different methods (ppmw)							Preferred method of removal	Comments
			Single stage wash	Three stage wash	acid wash	MHI and other agents wash	[1]UV/ O_3/ H_2O_2 method	Adsorption	Cooling/ cold wash		
Ammonia	Basic/-33-35	0.005 -10	0-6[41]	0-2[41]	1[42]		1[61,62]	1	30[42]	Acid scrubbing	Superscript is reference.
MEA	Basic/170.4	43-100[42]	10-25[41]	8-11[41]	0[42]	0.2[47,43]	4-10 [61,62]	4-10	0-0.7[42]	Acid scrubbing	Superscript is reference
Group of nitrosamines	Basic	6 – 70*	-	-	0[42]	-	0.7-14[61,62]	0.5-7	0-0.3[42]	Acid scrubbing	Superscript is reference
N-acetylethanolamine, $C_4H_9NO_2$	Basic/116-167	-	-	-	-	-	-	-	-	Acid scrubbing	No emission data available
N-glycylglycine, $C_4H_8N_2O_3$	Basic/453	-	-	-	-	-	-	-	-	Acid scrubbing	High boiling point
N-(hydroxyethyl)-succinimide, $C_6H_9NO_3$	Basic/160-164	-	-	-	-	-	-	-	-	Acid scrubbing	No emission data available
1-(2-hydroxyethyl)-2-imidazolinone, $C_6H_{10}N_2O_2$	Basic	0.0003	0	0	0	-	-	0	0	Acid scrubbing	Anticipated performance*
1-(2-hydroxyethyl)-2-imidazolidone (HEIA)[37], $C_6H_{11}N_2O_2$	Basic	-	-	-	-	-	-	-	-	Acid scrubbing	May react with acid
N-(2-hydroxyethyl)-ethylenediamine (HEEDA)[37], $C_4H_{13}N_2O$	Basic/140	0.02-1	0-0.6	0-0.2	0-0.1	-	-	0-0.1	0-0.1	Acid scrubbing	Anticipated performance*
N,N'-di(hydroxyethyl)urea (DHU)[37], $C_7H_{14}N_2O_3$	Basic	0-1	0-0.06	0-0.2	0-0,1	-	-	0-0.1	0-0.1	Acid scrubbing	Anticipated performance*
N,N-diacetylethanolamine, $C_6H_{11}NO_3$	Basic/133-135	0-2	0-0.12	0-0.4	0-0.2	-	-	0-0.1	0-0.1	Acid scrubbing	Anticipated performance*
Acetic acid, $C_2H_4O_2$	Acidic/116-117	0-4	-	-	-	-	-	-	-	Not required[1]	Will react with amine
Propionic acid, $C_3H_6O_2$	Acidic/141	-	-	-	-	-	-	-	-	Not required[1]	Will react with amine
N-butyric acid, $C_4H_8O_2$	Acidic/163-165	-	-	-	-	-	-	-	-	Not required[1]	Will react with amine
2,6-dimethyl-4-pyridinamine, $C_7H_{10}N_2$	Basic	-	-	-	-	-	-	-	-	Acid scrubbing	May react with acid
2-imidazolecarboxaldehyde, $C_5H_6N_2O$	Acidic	-	-	-	-	-	-	-	-	Not required[1]	Will react with amine
2-Oxazolidone (OXA), $C_3H_5NO_2$	Basic/220	0-0.05	0-0.01	0-002	0.001	-	-	0-0.005	0-0.005	Acid scrubbing	Anticipated performance*
Performance rating (0 to 10 for worse to best)			3	4	9	6	5	5	3		

**Pure guess without any reference to actual performance data which was not available for the emission removal from MEA process*

Properties and separation techniques of some compounds such as 1-(2-hydroxyethyl)-2-imidazolinone, $C_6H_{10}N_2O_2$, N-(2-hydroxyethyl)-ethylenediamine (HEEDA), $C_4H_{13}N_2O$, N,N'-di(hydroxyethyl)urea (DHU), and $C_7H_{14}N_2O_3$, N,N-diacetylethanolamine, $C_6H_{11}NO_3$ etc. are not available in the literature. Therefore their separation is anticipated (purely guessed) assuming that their concentrations in the gas stream after treatment by various methods could be anywhere between zero and their maximum initial concentrations as shown in Table 13. Further investigation will be required to determine the effectiveness of the methods of separating these compounds.

Table 14 Anticipated effectiveness of the separation of fine droplets from the CO_2-lean gas flue gas stream by various methods (based on anticipated inlet droplet content of 0.13 ppmv as referred earlier in the report)

Separating device/method	**Rated maximum efficiency (%)**		**Anticipated pressure drop range (mm WG)**	**Applicability (Rated 0 to 10 for worse to best)**	**Comments**
	Droplets <5 µm	**Droplets >5 µm**			
Vane demister, VH-2	45	45-99	20 -80	4	May not achieve the desired separation
Flexichevron vane type demister	45	45-99	0.2-100	4	May not achieve the desired separation
Wire mesh demister	70-92	99.9	0.1-100	5	Could be applicable, economical if optimized.
Swirl Mist Eliminator (SME)	99.9	>99.9	100-300	9	High cost to keep pressure drop low
Multicyclone	0	70	250-750	3	Poor efficiency and high pressure drop & cost
Brownian candle	94-100	100	50-500	7	High cost to keep pressure drop low
Impaction candle	60-100	100	100-250	5	Could be applicable, economical if optimized.

Emission as fine droplets could be effectively controlled by Swirl Mist Eliminators (SME) due to its high efficiency of separation for fine droplets and low pressure drop, as rated in Table 14. Brownian candles are also good but as they offer more pressure drop, consequently larger flow area requirement may escalate the installation costs. Wire mesh demisters could be very economical and effective if optimized to be effective for fine droplets. Both Brownian candle and wire mesh demisters could fail completely in the situation of flooding or over loading as there are no drainage channels which are isolated from the main stream of fluid passing through the device. Such situations are quite likely during startup or shut down, malfunctioning or any loss of control of the unit. The SME and vane type demisters have the advantage of isolated channels to allow quick drainage during overloading. However, due to their relatively low efficiency vane type demisters may not be suitable for emission control in the PCC application.

3.6 Scope for improving the current state-of-the-art

In order to be commercially viable, an ideal device or method for capturing gaseous and droplet emissions should also meet a set performance criteria for the power plants to which they will be fitted. These criteria are generally designed to prevent unscheduled shut downs which may be caused due to failure of any components or utilities of the unit and thus it allows for all maintenance and repairs to be carried out during annual shutdown of the power plant. The following performance criteria were developed on the basis of generally known design principles related to power generation processes:

1. The devices or methods should be able to continuously capture all gaseous and droplet emissions and meet the local environmental regulations.
2. The energy consumption and corresponding CO_2 emission should be low.
3. Retrofit should be possible without significantly altering the performance of PCC and power plant.
4. The availability factor should be above 95% or suitable to match with the power plant scheduled shutdowns
5. Must be scalable to suit capacities of PCC units.
6. Must be applicable to capture other emissions which might arise from different fuel or improved PCC process.

Based on Tables 13 and 14, Table 15 presents a performance rating for each technology. The major advantages and limitations of each technology are highlighted and the overall state of readiness for deployment is described. (Note Table 15 also refers to an anticipated timeframe to demonstration scale. This will be described subsequently).

Acid wash seems to be a reasonably developed technology but needs some developmental work for effective recycling of acid and recycling of captured amine and amine products. Weak acid such as CO_2 could be used for easy recyclability of acid (CO_2) and to minimise corrosion on equipment. However, CO_2 may require operation at slightly higher pressure to have sufficient concentration of CO_2 in wash water and operation at higher pressure above certain allowable operating pressure may not be feasible as it may require redesigning of the PCC process and equipment.

UV, plasma and oxidative degradation methods may not be effective for other chemicals except nitrosamines and some other amines. Therefore an integration of UV method with acid wash may be desired for effective removal of all species but some research will be required to develop methods for disposing/using the products resulting from UV and other oxidative processes.

Adsorption methods are well known for removing volatile organic compounds[70]. In this application, adsorption method could be used after identification or development of suitable adsorbents. Optimisation of cycle time with appropriate dehumidification measures will be useful in reducing the size and costs.

Cooling processes are well proven at industrial scale and could have very high throughput rate per unit volume of the equipment. This method is only suitable for the condensable vapours and therefore may not be quite suitable for traces of ammonia which has a condensation temperature below -33.35 ^{o}C unless the flue gas is cooled below -33 ^{o}C. However, it is to be ensured that water vapour is condensed out prior to cooling below 0 ^{o}C to avoid significant ice formation during further cooling. Also the cooling below -33 ^{o}C will be very energy intensive therefore may not be feasible unless cooling is produced from waste heat of solar energy.

Amongst the droplet emission control methods, the resizing and optimisation of Swirl Mist Eliminator to reduce its dimensions to fit within the diameter of an absorber column seems to be sufficient to integrate this unit with the absorber. Brownian candles to be further developed to have a fast drainage system to prevent their saturation during flooding. Brownian candle, Flexichevron demister, VH-2 demister and wire mesh demister need modifications and further optimisation to suite their application to PCC unit.

3.7 Expected improvements in future

The following are two areas where further work may significantly reduce the emissions from PCC units.

3.7.1 Correct optimisation of demisters

As a conventional design practices, the current absorption and stripper tower are designed to achieve highest mass transfer rate. This means sufficiently high gas and liquid velocities are maintained. Appropriate demisters are installed to coalesce fine droplets which result from the mixing of gas and liquid streams at reasonably high velocities in these columns. However, these demisters are fitted within these columns and therefore they have the same diameter as the columns but relatively less flow area than the gas space available in the column.

Conventional demister designs are based on Souder-Brown equation[81] (Equation 17 as described in section 3.4.1), as shown in the earlier section. The factor $K=0.35$, recommended for the conventional economic designs, may not be suitable to meet the emission standard and $K<0.35$ may be required to completely eliminate the liquid entrainment into the vent gases. It is to be noted that some demisters, based on this logic, have already been designed with $K = 0.12$. It is to be noted the optimum range of K value depends on the type of demister pad. The designs based on K factors beyond this range may have poor separation efficiency. For example at lower than the optimum velocities droplets may have lower momentum for impingement and coalescence by direct impingement mechanism and may be carried away with the gas phase unless it is trapped by Brownian or inertial impaction. The gas stream at velocity higher than the optimum range may have sufficient kinetic energy to re-entrain the liquid phase as fine droplets.

On the basis of these arguments, depending on the operating conditions and the type of demister the optimum diameter of the demister pad may have to be increased by up to 10 to 50% to have effective separation of fine droplets at sufficiently low pressure drop across the pad. This does not necessarily mean that the pad diameter will be 10 to 50% bigger than the absorption column diameter. In fact an integrated design approach for absorber and demister with proper selection of demister type will result in a feasible design. The pressure drop across the conventional demister is usually vary in the range of 0.1-750 mm WG as shown in Table 14, and most of the demisters are designed with pressure drop below 25 kPa. The integrated optimisation of absorber and demister pad to achieve lower values of K will further reduce the pressure drop across the demister.

Further research on the column design and optimization will be quite important from the emission point of view.

3.7.2 Minimising degradation and emission of liquid degradation products

The amine and its degradation products are the main source of emission and an ideal approach will be to minimise the degradation of MEA solution and keep it free from the degradation products which could be directly emitted as fine liquid droplets. Therefore by periodically removing the degradation products from the amine solution the emission could be indirectly minimised. A number of technologies reported in the literature could be further developed to remove the degradation products and then either recycled as parent amine, disposed or used elsewhere. These are based on ion exchange[76] , vacuum distillation[82], scrubbing with alkali[83], electrophoresis[84], electrodialysis (ED)[82,85], integrated ED with other conventional separation techniques (distillation, extraction etc.)[86,87,88,89,90,91,92], advanced membrane processes[93,94,95,96,97,98,99,100,101,102,103], and with biochemical processes [86,104,105] for chemical waste recycling.

Table 15 Summary of anticipated further development of the-state-of-the-art (🔴 Not required, ○ Required, ● Achieved, PC Proof of concept, LS laboratory scale, PS pilot Scale, DS Demonstration scale. Assumed timeframe 3 years/each stage PC, LS, PS or DS)

	Methods	Main limitations	Scope for improvement	Scalability challenge	Scaled up operation issues	Commercial Viability (0 least to 10 most)	Anticipated development track				Anticipated timeframe to demo. scale (years)
							PC	LS	PS	DS	
Gaseous emission control	Single stage wash	High MEA level in wash water	Larger wash water flow	Include large wash section	High water usage and recycle costs	0	🔴	🔴	🔴	🔴	0
	Three stage wash	High wash water flows	Addition of more stages	Could be added on top	Additional cost of recycling	2	○	○	○	○	12
	Acid wash	Acid, reclaimer, corrosion	Consider easily reclaimable weak acids	Reclaimer could be developed	Additional energy usage	8	●	○	○	○	9
	MHI, AKER, Others wash	No authentic performance data available	Thorough testing of the agents	-	-	-	●	●	○	○	6
	UV/oxidative	May not remove all chemicals	Extend to remove other chemicals	Could be scaled and retrofitted	Recycle/use destruction products	5	●	○	○	○	9
	Adsorption	Large size, cost	Cost and size reduction by new sorbents	Scale up with short cycles	Purge gas emission	6	○	○	○	○	12
	Cooling	Not suitable for gases	Reduce cooling energy demand	Very large energy demand	Recycling of condensate	3	○	○	○	○	12
Droplets emission control	VH-2 vane Demister	Poor efficiency	High efficiency design	Optimised K factor	Fouling	3	○	○	○	○	8
	Flexichevron vane demister	Poor efficiency	High efficiency design	Optimised K factor	Fouling	3	○	○	○	○	8
	Wire mesh demister	Saturation	Fast isolate draining mechanism	Optimised K factor	Fouling and pressure drop	5	○	○	○	○	8
	Swirl Mist Eliminator	Pressure drop	Reduce pressure drop	Integration with absorber	Fouling and pressure drop	8	○	○	○	○	8
	Multicyclone	Poor efficiency	Improve efficiency	Integration with absorber	Fouling	1	🔴	🔴	🔴	🔴	0
	Brownian candle	Saturation	Isolated draining mechanism	Optimised K factor	Fouling and pressure drop	6	○	○	○	○	8
	Impaction candle	Poor efficiency, saturation	Improve efficiency	Optimised K factor	Fouling and pressure drop	4	○	○	○	○	8

3.8 Anticipated timeframe and stages of development

As shown in Table 15, the methods which are less likely to be viable are less likely to be developed any further. Assuming about 2 and 3 years, respectively for droplet and gaseous emission respectively, required to cross each of stage of development from proof-of-concept through laboratory and pilot scale testing to the demonstration scale, the anticipated timeframe for the development of each method is estimated.

Acid wash and UV methods have already been proven concepts and it is anticipated to take another 9-10 years for demonstration scale development. The rest of the gaseous emission control methods may take over 12 years as they have not been even proven at the laboratory scale for PCC applications.

In case of droplet removal methods, none of the methods have been optimised and tried even at the laboratory scale for MEA systems and assuming about 2 years for each stage of development and testing about 8 years are required to prove these methods at demonstration scales. It is to be noted that some of these methods may not be able to cross all of the developmental stages.

4 HSE REGULATIONS FOR CHEMICAL EMISSIONS

Emissions of different pollutants from industrial sources are regulated by Standards and Limits to reduce or control the potential impacts of pollutants on human health and the environment. These industries are required to regularly report on their emissions as stated in their permitting licences. The identification and quantification of major emissions and the reporting of these values to the appropriate authority are considered as a core activity to demonstrate the environmental performance of the plant.

Emissions from PCC plants may contain chemical substances related to the used amines and their degradation products that are toxic or may raise different environmental concerns. Consequently, industrial-scale PCC systems will be subject to pollution mitigation regulation. Currently, little is known about the health risks related to amines that are expected to be emitted from PCC. Most countries have legislations that regulate emissions of common pollutant species, especially for the following “criteria” pollutants, which are considered as the measure of pollution in air. These are ozone, carbon monoxide, sulphur dioxide, nitrogen dioxide, lead and particulate matter as these are commonly found in the air. These pollutants have been regulated by developing human health-based and/or environmentally-based criteria for setting permissible levels. The set of limits based on human health is called primary standards. Another set of limits intended to prevent environmental and property damage is called secondary standards.

Most countries have legislation that regulates emissions of common pollutant species, especially the six so called criteria pollutants: ozone, carbon monoxide, sulphur dioxide, nitrogen dioxide, lead and particulate matter and ozone. Out of these pollutants ozone is not likely to be produced directly in the PCC process but it may be produced by secondary atmospheric chemical reactions. In addition to the criteria pollutants there are a large number of other toxic materials that are of concern globally. In the United States, more than 180 substances have been classified as hazardous air pollutants (HAPs)[106] and similar lists have been adopted in many other countries. Regulatory agencies throughout the world either have already developed, e.g. the US, or are now actively developing rules for industry and other sources to minimise emissions of these materials. Some of the compounds that have been identified as potential atmospheric emissions from PCC units are classified as HAPs.

In this section the available health, safety and environmental (HSE) regulations that may be relevant to these emissions from amine-based CO_2 capture PCC processes are examined.

The overall objectives of this section were to:

- Identify the range of compounds that may be emitted from PCC units that are already subject to regulation.
- Where available, assess the anticipated permissible levels of these chemicals in ambient air.
- Identify gaps in the HSE regulations related to PCC process emissions.

Although the hypothetical PCC unit considered in this report is assumed to be based in the Netherlands, we have broadened the examination of the relevant standards from other parts of the world.

4.1 PCC Emissions

Direct measurements of atmospheric emissions from full-scale amine PCC systems are as yet unavailable, although laboratory-scale and modelling investigations have been conducted to determine the type of materials likely to be present in the emissions from the future units[107,108]. These studies suggest PCC emissions will contain some of the alkanolamine solvent along with various degradation products which may include amines, ammonia, amides, carbonyls and nitrosamines. Some of the degradation products can accumulate over time because they are stable while others can undergo further chemical reactions to produce other chemical compounds, which could be distinguished based on their volatility where heavier compounds are not expected to be emitted with the same rate as that of lighter compounds which usually have a higher volatility.

Table16 Compounds that may be present in emissions from an amine PCC unit

Class	**Compounds***	**CAS Number**
PCC solvents	Monoethanolamine (MEA)	141-43-5
	Diethanolamine (DEA)	111-42-2
	2-Amino-2-methyl-1-propanol (AMP)	124-68-5
	Piperazine	110-85-0
	N-Methyldiethanolamine (MDEA)	105-59-9
Amines	Ammonia	7664-41-7
	Ethylamine	75-04-7
	Methylamine	74-89-5
	Dimethylamine	124-40-3
	Diethylamine	109-89-7
	N-Methylethylamine	624-78-2
	1-Propanamine	107-10-8
	1,2-Ethanediamine	107-15-3
Amides	Formamide	75-12-7
	Acetamide	60-35-5
	N-(2-Hydroxyethyl) formamide	693-06-1
	N-(2-Hydroxyethyl) acetamide	142-26-7
	N-Methylformamide	123-39-7
Aldehydes	Formaldehyde	50-00-0
	Acetaldehyde	75-07-0
	2-aminoacetaldehyde	6542-88-7
	Hydroxyacetaldehyde	141-46-8
Alcohols	Ethanol	64-17-5
	1,2-Ethanediol	107-21-1
Acids	Formic acid	64-18-6
	Acetic acid	64-19-7
	Propanoic acid	79-09-4
	Butanoic acid	107-92-6
	Glycolic acid	79-14-1
Nitrosamines	*N*-Nitrosodimethylamine (NDMA)	62-75-9
	N-Nitrosodiethylamine (NDEA)	55-18-5
	N-Nitrosomorpholine (NMor)	59-89-2
	N-Nitrosopiperidine (NPip)	100-75-4
	N-Nitrosodiethanolamine (NDELA)	1116-54-7
	N-Nitrosopiperazine (NPz)	5632-47-3
	1,4-Dinitrosopiperazine	140-79-4

** the list is comprehensive based on literature information and possibilities of more compounds could not be ignored. This list does not contain compounds produced as a result of degradation in the atmosphere.*

It is to be noted that the flue gas is desulphurised prior to being subjected to CO_2 separation. This is mainly to limit the degradation of MEA by SO_x, and therefore prevent or minimise emissions of SO_x and MEA degradation products into the atmosphere.

A summary of some of the anticipated emission species derived from the various amine based solvents is shown in Table 16. Although this is not an exhaustive list, the compounds which are most likely to be present in the emission are included.

The compounds listed in Table 16 provide the basis for the examination of the various emissions standards considered in this report.

4.2 Hazardous Levels of emissions in Air

Exposure to hazardous chemicals in air is normally regulated by either ambient air quality standards or occupational exposure limits. Ambient air quality limits are intended to protect the general population from air pollution and hence are set as low as possible to avoid adverse effects in the most vulnerable individuals. Occupational exposure limits (OELs), on the other hand, are designed to minimise the exposure of healthy adult workers to toxic substances in the workplace. Because of the wide range of industrial chemicals in use, occupational exposure standards exist for many materials, whereas ambient guidelines usually apply to a much smaller range of common hazardous pollutants (mostly the criteria pollutants).

In both ambient and occupational standards, the exposure limits are expressed as a time-weighed-average (TWA) value where the maximum permissible concentration is the average concentration over a specified time period. Often, several averaging periods may be specified, ranging from as little as 10 minutes up to one year, with progressively lower concentrations allowed over longer periods. For example, the World Health Organisation's Air Quality Guidelines for Europe suggest limits for SO_2 of 500 μg m^{-3} over 10 minutes, 125 μg m^{-3} over 24 hours and 50 μg m^{-3} over 1 year[109]. It is important to note that significantly higher concentrations of the pollutant are permissible for short periods, provided that the average concentration remains below the specified limit. In recognition of this, ambient standards frequently specify a maximum number of exceedences throughout each year.

Occupational exposure standards usually have TWA periods that correspond to an 8-hour (or sometimes 10-hour) shift but 15-minute short term exposure limits (STEL) may also be applicable. Because of the shorter exposure times, and the fact that they are intended to protect healthy adults, occupational limits may be higher than the corresponding ambient standards. This is illustrated with SO_2 where the US occupational TWA limit over 8 hours is 5 mg m^{-3} and the STEL is 13 mg m^{-3} over 15 minutes; both of which are many times higher than SO_2 ambient air quality guidelines shown above.

In almost all standards, both ambient and occupational, the units of concentration are expressed in either parts per million (ppm) or mg m^{-3} or sometimes both. Concentrations in ppm at one atmosphere can be converted to mg m^{-3} according to the following expression:

$$Conc\,(mgm^{-3}) \;=\; Conc\,(ppm)\; x\; \frac{MW}{22.414\,x\,(273.15+T)/273.15} \qquad (18)$$

Where, *MW* is the molecular weight of the compound and *T* is the reference temperature (usually 20 °C or 25 °C).

4.3 International Standards

4.3.1 Current Emission Standards

Emission standards relate to the amount of a pollutant that can be discharged from a particular facility, such as a power station. Most industrial facilities are subject to some form of emissions regulation. In the United States for example, a range of pollutants such as SO_2, NO_x, particulate matter and various others are regulated under the New Source Performance Standard which sets the amount of material that can be emitted from new stationary sources. The US also has established emission standards for stationary sources for designated Hazardous Air Pollutants – the National Emission Standards for Hazardous Air Pollutants Compliance Monitoring (NESHAP). Under this scheme, rather than setting absolute emission targets for each pollutant, regulators require individual facilities emitting these compounds to apply the Maximum Achievable Control Technology to minimise emissions.

In the EU, industrial emissions are addressed under the Directive on Integrated Pollution Prevention and Control[110] which is intended to minimise industrial pollution generally. Like the American NESHAP this Directive does not specify emission limits. Instead, European member states are required to ensure that when operating permits are issued to individual installations, appropriate limits are set according to Best Available Techniques.

As well as emission standards for individual industrial facilities, emission standards may apply to certain regions to minimise transboundary pollution. Transboundary pollution is an important environmental issue and is currently addressed by the 1979 Geneva Convention on Long-range Transboundary Air Pollution. This convention includes a number of protocols intended to cover specific pollutants. Relevant to emissions from amine units is the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (Gothenburg Protocol). Under this protocol, signatories are required to reduce and maintain the reduced levels of pollutants to agreed levels.

In response to this protocol the European Union has issued Directive 2001/81/EC that set limits for the amounts of pollutant species that can be emitted in individual countries[110]. This directive is designed to reduce emissions of:

- Sulphur dioxide
- Nitrogen oxides
- Volatile organic compounds
- Ammonia.

Total annual emissions (in kilotonnes) of each pollutant are defined in the Directive for each member country as shown in Table 17.

Emissions from PCC units may affect the emission inventories for some of these compounds. On the one hand, emissions of NO_x and SO_2 from stationary power generation sources equipped with amine PCC systems will probably be substantially lower, although as noted above at least one study has indicated that NO_x may actually increase as a result of PCC[112]. VOCs and NH_3 on the other hand are likely to increase when PCC is applied. At present there are relatively few quantitative data relating to PCC unit emissions so the effect on emission inventories cannot be accurately estimated. Nevertheless, there are some data from pilot scale processes that can help to assess the relative magnitude of these emissions. In a recent study reported for a pilot unit operating with a lignite fired power generation plant in Germany, NH_3 emissions were measured to estimate MEA emissions[9]. That study suggested that between about 0.09 and 0.16 kg of NH_3 was emitted per tonne of CO_2 captured.

Table 17 EU annual emission limits for each country[110].

Country	**SO_2 (kt)**	**NO_x (kt)**	**VOC (kt)**	**NH_3 (kt)**
Belgium	99	176	139	74
Bulgaria	836	247	175	108
Czech Republic	265	286	220	80
Denmark	55	127	85	69
Germany	520	1051	995	550
Estonia	100	60	49	29
Greece	523	344	261	73
Spain	746	847	662	353
France	375	810	1050	780
Ireland	42	65	55	116
Italy	475	990	1159	419
Cyprus	39	23	14	9
Latvia	101	61	136	44
Lithuania	145	110	92	84
Luxembourg	4	11	9	7
Hungary	500	198	137	90
Malta	9	8	12	3
Netherlands	50	260	185	128
Austria	39	103	159	66
Poland	1397	879	800	468
Portugal	160	250	180	90
Romania	918	437	523	210
Slovenia	27	45	40	20
Slovakia	110	130	140	39
Finland	110	170	130	31
Sweden	67	148	241	57
UK	585	1167	1200	297

To put these figures into perspective it is instructive to compare them with the ceiling values of Directive 2001/81/EC. During 2008, the total CO_2 emissions from the 27 EU countries associated with public electricity and heat production was about 1341 Mt (European Environment Agency, 2010). Assuming that all of this CO_2 is to be captured in amine-based PCC units, emissions would be between 117 and 205 kt NH_3 per annum. This represents about 5 % of the annual combined ceiling emissions of 4294 kt of NH_3 for the 27 countries shown in Table 17.

Although a relatively small component of the total European NH_3 emissions, the distribution of PCC units throughout the region may result in significantly higher nitrogen loads at the local scale. Emissions should also be set against the context of continuing efforts to reduce air pollution in general. The European Union currently has a “Thematic Strategy on Air Pollution” which is designed to supplement current legislation. The aim of this strategy is to make large cuts in emissions of a number of pollutants, including NH_3, by 2020. It is likely therefore that emissions from PCC units will come under closer public scrutiny as attempts to meet these targets progress.

4.3.2 Ambient Air Quality Standards

Air quality standards are quite distinct from emission standards described in the preceding section since they refer to the concentration of a given pollutant in ambient air rather than emissions from individual facilities. However, the two are indirectly related because emission standards may be set to achieve air quality goals.

There are numerous ambient air quality guidelines throughout the world, many of which are adopted in relevant environmental protection legislation. In Europe as well as in other parts of the world, the World Health Organisation's Air Quality Guidelines for Europe have formed the basis of the air quality standards adopted by many countries. These guidelines include recommended maximum exposure limits for a range of substances, although most of the legislated ambient air quality standards set concentration limits for a subset of these materials; usually the six criteria pollutants and perhaps a few other HAPs. In Table 18, the WHO recommended exposure limits along with a selection of various international ambient air quality standards are shown. In the European Union, member countries are expected to abide by Directive 2008/50/EC, which specify air quality standards for ozone, SO_2, NO_2, CO, lead, PM_{10}, $PM_{2.5}$ and benzene. Additional EU air quality standards relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons are defined in Directive 2004/107/EC.

The EU Directives are provided as minimum requirements but member states may adopt tighter standards if required. In the United Kingdom, for example, the 8-hour limit for ozone is 100 $\mu g\ m^{-3}$ whereas the EU requirement is 120 $\mu g\ m^{-3}$. There may also be different limits for more sensitive areas. Again in the UK, some of the limits for Scotland and other regions are lower than the overall national targets.

Table 18 also shows the National Ambient Air Quality Standards implemented in the United States under the Clean Air Act. The US standards are broadly similar to the European standards although there are several significant differences. In the US regulations, the PM_{10} standard is substantially higher than the corresponding European limit, but for $PM_{2.5}$, the US requirement is lower.

The United States also has state legislation that although consistent with the federal requirements, may impose more stringent requirements. Most notable is California, which has among the most rigorous air quality standards in the world.

As well as the TWA limit values for particular pollutants, standards may also specify the number of occasions when these threshold values may be exceeded within one year[106]. In the EU SO_2 standards, the hourly 350 $\mu g\ m^{-3}$ limit may be exceeded up to 35 times in a year, whereas for the 24-hour limit of 125 $\mu g\ m^{-3}$ only three excedences are permitted. Permissible annual exceedences are also specified for NO_2 (18 for the hourly limit) and PM_{10} (35 for the 24-hour limit).

It is clear from Table 18 that existing air quality standards do not generally include those compounds likely to be associated with PCC emissions. Despite this, broader legislative requirements for industry to reduce emissions ,may be relevant, e.g. the EU, for example, the Directive on Integrated Pollution Prevention and Control[110] and, the United States federal regulations, These regulations require industry to eliminate or minimise emissions of the identified HAPs including diethanolamine, acetamide, formaldehyde, acetaldehyde, N-nitrosodimethylamine and N-nitrosomorpholine, as listed in Table 16. These more general regulations are very likely to affect the operation of amine based PCC units.

In the cases were flue gas desulphurisation (FGD) and selective catalytic reduction (SCR) is not used in the power plant, NO_2 and SO_2 will probably also be removed by reaction with the basic amine in the unit. However, it has been estimated[112] that due to the reduced overall efficiency of PCC-equipped power plants, total NO_x emissions may increase (presumably as NO since most NO_2 would be removed by the amine solvent). While the other criteria species are not likely to be significant primary emissions, it may be that some of the other materials emitted from a PCC system may subsequently react to produce different secondary pollutants. Amines, for example may react to form secondary products such as secondary aerosols, ozone, NH_3 and N-nitroso compounds.

Table 18 Air quality standards for Europe and the United States

	Averaging Time	**World Health Organisation**	**European Union**	**Germany**	**United Kingdom**	**United States**
Ozone	1 hour	-	-		-	-
	4 hours	-	-		-	-
	8 hours	120 μg m^{-3}	120 μg m^{-3}	120 μg m^{-3}	100 μg m^{-3}	147 μg m^{-3}
CO	15 minutes	100 mg m^{-3}	-		-	-
	1 hour	30 mg m^{-3}	-		-	40 mg m^{-3}
	8 hours	-	10 mg m^{-3}	10 mg m^{-3}	10 mg m^{-3}	10 mg m^{-3}
SO_2	15 minutes	500 μg m^{-3} (10 min average)	-		266 μg m^{-3}	-
	1 hour	-	350 μg m^{-3}	350 μg m^{-3}	350 μg m^{-3}	196 μg m^{-3}
	24 hours	125 μg m^{-3}	125 μg m^{-3}	125 μg m^{-3}	125 μg m^{-3}	-
	1 year	50 μg m^{-3}	-	50 μg m^{-3}	-	-
NO_2	1 hour	200 μg m^{-3}	200 μg m^{-3}	200 μg m^{-3}	200 μg m^{-3}	188 μg m^{-3}
	1 year	40 μg m^{-3}	40 μg m^{-3}	40 μg m^{-3}	40 μg m^{-3}	100 μg m^{-3}
Lead	Calender quarter	-	-		-	1.5 μg m^{-3}
	1 year	0.5 μg m^{-3}	0.5 μg m^{-3}	0.5 μg m^{-3}	0.25 μg m^{-3}	-
PM_{10}	24 hours	50 μg m^{-3}	50 μg m^{-3}	50 μg m^{-3}	50 μg m^{-3}	150 μg m^{-3}
	1 year	20 μg m^{-3}	40 μg m^{-3}	40 μg m^{-3}	40 μg m^{-3}	-
$PM_{2.5}$	24 hours	25 μg m^{-3}				35 μg m^{-3}
	1 year	10 μg m^{-3}			25 μg m^{-3}	15 μg m^{-3}
Benzene	1 year	Not defined	5 μg m^{-3}	5 μg m^{-3}	16.25 μg m^{-3}	
PAH	1 year	Not defined	1 ng m^{-3}		0.25 ng m^{-3}	
1,3-Butadiene	1 year	Not defined			2.25 μg m^{-3}	
Arsenic	1 year	Not defined	6 ng m^{-3}			
Cadmium	1 year	5 ng m^{-3}	5 ng m^{-3}			
Nickel	1 year	Not defined	20 ng m^{-3}			
Manganese	1 year	0.15 μg m^{-3}				
Vanadium	24 hours	1 μg m^{-3}				
Mercury	1 year	1 μg m^{-3}				
1,2-Dichloroethane	24 hours	0.7 mg m^{-3}				
Dichloromethane	24 hours	3 mg m^{-3}				
	1 week	0.45 mg m^{-3}				
Formaldehyde	30 minutes	0.1 mg m^{-3}				
Hydrogen sulphide	24 hours	150 μg m^{-3}				
Styrene	1 week	0.26 mg m^{-3}				
Tetrachloroethylene	1 year	0.25 mg m^{-3}		10 μg m^{-3}		
	1 week	0.26 mg m^{-3}				

Since there are currently no ambient air quality standards relating specifically to most of the potential PCC emissions, there have been some investigations aimed at developing suitable emission criteria. In Norway, recent studies by the Norwegian Institute of Public Health examined the toxicity of a range of amine and related compounds and suggested a set of exposure guidelines for these compounds for the general population[4]. The suggested limits for each material are summarised in Table 19. As reported[3] a number of other compounds apart from those shown in Table 19 were examined. However, the authors concluded that there was insufficient data available to allow quantitative exposure limits to be set. Consequently, considerable further research is required in this area. This lack of data relating to human health effect of some potential PCC emissions has perhaps prompted Shao and Stangeland[4,111] to suggest that carbon capture and storage (CCS) demonstration projects "with amine based CO_2 capture can only receive public funding if they address research activities on environmental impact of amines and that "no full scale CO_2 capture units based on amines should be built before the knowledge gaps are filled".

Table 19 Suggested exposure guidelines for various amines and degradation products as suggested by Låg et al[3,111]

Compound	**Exposure Limit**
MEA	10 $\mu g\ m^{-3}$
Piperazine	5 $\mu g\ m^{-3}$
AMP	6 $\mu g\ m^{-3}$
MDEA	120 $\mu g\ m^{-3}$
Nitrosamines	0.3 ng m^{-3} (using NDMA to represent all nitrosamines)
Nitramines	0.3 ng m^{-3}

Most ambient air quality standards are set to protect human health, but atmospheric emissions can also affect the environment. Eutrophication and acidification of land and waterways are of particular concern and accordingly, some guidelines specify limits to protect vegetation (e.g. usually limits for NO_2 and SO_2). Many of the emissions from amine based PCC systems will contain nitrogen and have the potential to affect vegetation either by directly damaging plant material or by stimulating growth. The effects of nitrogen-containing air pollutants are considered in the WHO Air Quality Guidelines which recommend certain threshold values for various compounds. The WHO Guidelines are expressed as critical levels (CLE) which are defined as concentrations above which adverse effects to plants or ecosystems begin to become apparent. The CLEs for NO_x are 75 $\mu g\ m^{-3}$ averaged over a 24-h period and 30 $\mu g\ m^{-3}$ as an annual mean. For NH_3, the current CLE is 8 $\mu g\ m^{-3}$ as an annual mean; however, this value has recently been criticised as being too high[2]. In a study of the effects of ammonia on vegetation, Cape et al[2] found evidence from field observations in Europe that significant damage to vegetation occurs at levels well below the 8 $\mu g\ m^{-3}$ CLE. They suggest therefore that 1 $\mu g\ m^{-3}$ is more suitable for NH_3.

In Europe as in other parts of the world, transboundary pollution is an important environmental issue and is currently addressed by the 1979 Geneva Convention on Long-range Transboundary Air Pollution. This convention includes a number of protocols intended to cover specific pollutants. Relevant to emissions from amine units is the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (Gothenburg Protocol). Under this protocol, signatories are required to reduce and maintain the reduced levels of pollutants to agreed levels.

4.3.3 Occupational Exposure Limits

Most of the compounds expected to be emitted from an amine PCC unit are not covered by ambient air quality guidelines. However, some of these substances occur in industrial environments and are subject to regulation in workplaces throughout the world. Exposure of workers to toxic chemicals is usually managed by applying occupational exposure limits (OELs).

Historically, OELs were set according to levels that could be reasonably achieved using existing technology[9,112]. However, exposure limits are now often set at levels at which there are no observed adverse health effects[113]. For carcinogenic and mutagenic substances it is considered that there is no level below which there are no health effects, so health-based OELs are not assigned to these materials. Nevertheless, for practical purposes, OELs for some of these materials are provided in many jurisdictions.

One of the most influential organisations in the area of determining OELs is the American Conference of Governmental Industrial Hygienists (ACGIH)[114]. The ACGIH has over many years established threshold limit values (TLVs) for numerous chemical and physical agents which have been used throughout the world for setting legislated workplace OELs. However, these days, many countries have their own government organisations that provide scientific advice on setting appropriate workplace standards. For example, in the United States, the National Institute for Occupational Safety and Health (NIOSH)[115] is the statutory authority that develops and recommends occupational exposure standards. The US Occupational Safety and Health Administration (OSHA)[115], considers the NIOSH recommendations when setting the regulatory permissible exposure limits (PELs), although it is not obliged to accept the NIOSH recommendations.

In the European Union, member states are obliged to legislate to provide minimum standards of workplace safety. These standards include exposure limits for certain chemicals as outlined in a number of European Directives:

1. Directive 2009/161/EU - indicative occupational exposure limit values
2. Directive 2009/148/EC - exposure to asbestos at work
3. Directive 2006/15/EC - indicative occupational exposure limit
4. Directive 2004/37/EC - carcinogens or mutagens at work
5. Directive 2000/39/EC - indicative occupational exposure limit values
6. Directive 98/24/EC - risks related to chemical agents at work
7. Directive 91/322/EEC - indicative limit

Within these directives, (Directive 2000/39/EC and Directive 2006/15/EC), exposure levels have been documented for about 100 compounds, nine of which appear in Table 16.

Most of the OELs contained within the EU directives are indicative, that is they are not binding. Rather they are provided so that individual countries can take them into account when setting their mandatory exposure limits. As a consequence, there is a considerable range of exposure limits for compounds across different countries although there is some evidence suggesting that with successive national revisions, exposure limits within the European Union are tending to converge[116]. A summary of the European Union indicative OELs is shown in Table 20 along with the mandated workplace standards for several European countries. For comparison, the US NIOSH recommended OELs and the mandated OSHA PELs are also shown.

When determining exposure levels, the potential of the material to cause cancer in humans is normally considered. The International Agency for Research on Cancer (IARC)[117], maintains a database on more than 900 agents that have been evaluated with regard to their carcinogenicity and are classified into one of five categories:

- Group 1. The agent is carcinogenic to humans;
- Group 2A. The agent is probably carcinogenic to humans;
- Group 2B. The agent is possibly carcinogenic to humans;
- Group 3. The agent is not classifiable as to its carcinogenicity to humans (i.e. there is insufficient evidence to determine if the material causes cancer or not);
- Group 4. The agent is probably not carcinogenic to humans.

Some of the potential PCC emissions have been evaluated by the IARC and where available, the IARC classifications are shown in Table 20.

In general, the national exposure limits shown in Table 20 are the standards required by law in each country. However, in the Netherlands, the system for OELs includes public and private standards. The private OELs are industry-specific standards and in some cases there may be a number of these for the same chemical. The selection of standards listed in Table 20 show that for most of the substances that have been identified as potential PCC emissions, OELs already exist, albeit from a variety of jurisdictions. However, for nitrosamines, there are very few limits legislated apart from health-based OELs. These substances are of particular concern because of their toxicity and suspected carcinogenicity and thus further research will be required to develop appropriate health-based exposure limits. When considering the appropriateness or otherwise of existing standards, it must be remembered that at this stage, the composition of amine PCC emissions is largely speculative. Measurement of actual flue gas emissions may reveal a significantly different suite of compounds to those shown in Table 20. Therefore as more information becomes available, it will be necessary to reassess existing standards in light of the actual emissions.

4.3.4 Regulation of Industrial Chemicals

The chemical management system Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH)[118] in the countries within European Union may have implications for PCC unit operators in addition to the regulatory OELs. This regulation (EC 1907/2006) came into effect in 2007 and is intended to strengthen protection of the environment and human health by identifying hazardous properties of industrial chemicals. Under this regulation, the chemical manufacturers and importers are required to make available detailed information on hazards associated with their products to the European Chemical Agency (ECHA), which among other things, coordinate substance evaluations and maintain a publicly accessible database of all registered chemicals. The ECHA database contains relevant chemical hazard information including risk management advice that downstream users are required to follow when working with these chemicals. Registration of chemicals is required when quantities of more than 1 t are involved. However, certain “substances of very high concern” must be registered if they are present in a product at concentrations of more than 0.1 %. These substances are either very toxic or potent carcinogens. At present a number of potential amine solvents are registered with ECHA, including MEA, DEA, AMP and piperazine. However, since there are also many proprietary blends of solvents available, these would also need to be evaluated and registered prior to their deployment in Europe.

Table 20 Materials with their IARC rating and exposure limits

Compound	**IARC Rating**	**EU Directives**	**Netherlands**	**Germany**	**UK**	**Sweden**	**US - NIOSH**	**US - OSHA**
Monoethanolamine (MEA)	Not rated	1 ppm; 2.5 mg m^{-3}	1 ppm; 2.5 mg m^{-3} STEL : 3 ppm; 7.6 mg m^{-3}	2 ppm; 5.1 mg m^{-3}	1 ppm; 2.5 mg m^{-3} STEL : 3 ppm; 7.6 mg m^{-3}	3 ppm; 8 mg m^{-3} STEL : 6 ppm; 15 mg m^{-3}	3 ppm; 8 mg m^{-3} STEL : 6 ppm; 15 mg m^{-3}	3 ppm; 6 mg m^{-3}
Diethanolamine (DEA)	3		Various private OELs			3 ppm; 15 mg m^{-3} STEL : 6 ppm; 30 mg m^{-3}	3 ppm; 15 mg m^{-3}	
2-Amino-2-methyl-1-propanol (AMP)	Not rated							
Piperazine	Not rated	0.028 ppm; 0.1 mg m^{-3}			0.028 ppm; 0.1 mg m^{-3} STEL : 0.084 ppm; 0.3 mg m^{-3}	0.1 ppm; 0.3 mg m^{-3} STEL : 0.3 ppm; 1 mg m^{-3}		
N-Methyldiethanolamine (MDEA)	Not rated							
Ammonia	Not rated	20 ppm; 14 mg m^{-3} STEL : 50 ppm; 36 mg m^{-3}	20 ppm; 14 mg m^{-3} STEL : 50 ppm; 36 mg m^{-3}	20 ppm; 14 mg m^{-3}	25 ppm; 18 mg m^{-3} STEL : 35 ppm; 25 mg m^{-3}	25 ppm; 18 mg m^{-3} STEL : 50 ppm; 35 mg m^{-3}	25 ppm; 18 mg m^{-3} STEL : 35 ppm; 27 mg m^{-3}	50 ppm; 35 mg m^{-3}
Ethylamine	Not rated	5 ppm; 9.4 mg m^{-3}	5 ppm; 9 mg m^{-3}	5 ppm; 9.4 mg m^{-3}	2 ppm; 3.8 mg m^{-3} STEL : 6 ppm; 11 mg m^{-3}	10 ppm; 18 mg m^{-3} STEL : 15 ppm; 30 mg m^{-3}	10 ppm; 18 mg m^{-3}	10 ppm; 18 mg m^{-3}
Methylamine	Not rated		Various private OELs	10 ppm; 13 mg m^{-3} STEL : 10 ppm; 13 mg m^{-3}		10 ppm; 13 mg m^{-3} STEL : 20 ppm; 25 mg m^{-3}	10 ppm; 12 mg m^{-3}	10 ppm; 12 mg m^{-3}
Dimethylamine	Not rated	2 ppm; 3.8 mg	1 ppm; 1.8 mg	2 ppm; 3.7	2 ppm; 3.8	2 ppm; 3.5 mg	10 ppm; 18 mg m^{-3}	10 ppm; 18

		m^{-3} STEL : 5 ppm; 9.4 mg m^{-3}	m^{-3}	mg m^{-3}	mg m^{-3} STEL : 6 ppm; 11 mg m^{-3}	m^{-3} STEL : 5 ppm; 9 mg m^{-3}		mg m^{-3}
Diethylamine	Not rated	5 ppm; 15 mg m^{-3} STEL : 10 ppm; 30 mg m^{-3}	5 ppm; 15 mg m^{-3} STEL : 10 ppm; 30 mg m^{-3}	5 ppm; 15 mg m^{-3} STEL : 10 ppm; 30 mg m^{-3}	15 ppm; 3.8 mg m^{-3} STEL : 10 ppm; 30 mg m^{-3}	10 ppm; 30 mg m^{-3} STEL : 15 ppm; 45 mg m^{-3}	10 ppm; 30 mg m^{-3} STEL : 25 ppm; 75 mg m^{-3}	25 ppm; 75 mg m^{-3}
N-Methylethylamine	Not rated							
1-Propanamine	Not rated		Private STEL : 5 ppm; 12 mg m^{-3}					
1,2-Ethanediamine	Not rated		Various private OELs			10 ppm; 25 mg m^{-3} STEL : 15 ppm; 35 mg m^{-3}	10 ppm; 25 mg m^{-3}	
Formamide	Not rated		Various private OELs		20 ppm; 37 mg m^{-3} STEL : 30 ppm; 56 mg m^{-3}	10 ppm; 20 mg m^{-3} STEL : 15 ppm; 30 mg m^{-3}	10 ppm; 15 mg m^{-3}	
Acetamide	2B		Private 10 ppm; 25 mg m^{-3} STEL : 25 ppm; 60 mg m^{-3}			10 ppm; 25 mg m^{-3} STEL : 25 ppm; 60 mg m^{-3}		
N-(2-Hydroxyethyl) formamide	Not rated							
N-(2-Hydroxyethyl) acetamide	Not rated							
N-Methylformamide	Not rated		Private but not limits set					
Formaldehyde	1		0.1 ppm; 0.15	0.3 ppm;	2 ppm; 2.5	0.5 ppm; 0.6	0.016 ppm; 0.02	0.75 ppm; 0.9

			mg m^{-3} STEL : 0.4 ppm; 0.5 mg m^{-3}	0.37 mg m^{-3} Ceiling : 1 ppm; 1.2 mg m^{-3}	mg m^{-3} STEL : 2 ppm; 2.5 mg m^{-3}	mg m^{-3} Ceiling : 1 ppm; 1.2 mg m^{-3}	mg m^{-3} Ceiling : 0.1 ppm; 0.12 mg m^{-3}	mg m^{-3} Ceiling : 2 ppm; 2.5 mg m^{-3}
Acetaldehyde	2B		20 ppm; 37 mg m^{-3} STEL : 50 ppm; 92 mg m^{-3}	50 ppm; 91 mg m^{-3} Ceiling : 100 ppm; 180 mg m^{-3}	20 ppm; 37 mg m^{-3} STEL : 50 ppm; 92 mg m^{-3}	25 ppm; 45 mg m^{-3} STEL : 50 ppm; 90 mg m^{-3}		200 ppm; 360 mg m^{-3}
2-aminoacetaldehyde	Not rated							
Hydroxyacetaldehyde	Not rated							
Ethanol	1 (Note: this rating refers to ethanol in alcoholic beverages. Occupational exposure is generally considered to be a low cancer risk provided doses are below the OEL)		138 ppm; 260 mg m^{-3} STEL : 1000 ppm; 1900 mg m^{-3}	500 ppm; 960 mg m^{-3}	1000 ppm; 1920 mg m^{-3}	500 ppm; 1000 mg m^{-3} STEL : 1000 ppm; 1900 mg m^{-3}	1000 ppm; 1900 mg m^{-3}	1000 ppm; 1900 mg m^{-3}
1,2-Ethanediol	Not rated	20 ppm; 52 mg m^{-3} STEL : 40 ppm; 104 mg m^{-3}	20 ppm; 52 mg m^{-3} STEL : 41 ppm; 104 mg m^{-3}	10 ppm; 26 mg m^{-3}	20 ppm; 52 mg m^{-3} STEL : 40 ppm; 104 mg m^{-3}	10 ppm; 25 mg m^{-3} STEL : 20 ppm; 50 mg m^{-3}		
Formic acid	Not rated	5 ppm; 9 mg m^{-3}	STEL : 2.6 ppm; 5 mg m^{-3}	5 ppm; 9.5 mg m^{-3}	5 ppm; 9.6 mg m^{-3}	3 ppm; 5 mg m^{-3} STEL : 5 ppm; 9 mg m^{-3}	5 ppm; 9 mg m^{-3}	5 ppm; 9 mg m^{-3}
Acetic acid	Not rated		Various private OELs			5 ppm; 13 mg m^{-3} STEL : 10	10 ppm; 25 mg m^{-3} STEL : 15 ppm; 37 mg m^{-3}	10 ppm; 25 mg m^{-3}

						ppm; 25 mg m^{-3}		
Propanoic acid	Not rated	10 ppm; 31 mg m^{-3} STEL : 20 ppm; 62 mg m^{-3}	10 ppm; 31 mg m^{-3} STEL : 20 ppm; 62 mg m^{-3}	10 ppm; 31 mg m^{-3}	10 ppm; 31 mg m^{-3} STEL : 15 ppm; 46 mg m^{-3}	10 ppm; 30 mg m^{-3} STEL : 15 ppm; 45 mg m^{-3}	10 ppm; 30 mg m^{-3} STEL : 15 ppm; 45 mg m^{-3}	
Butanoic acid	Not rated							
Glycolic acid	Not rated							
N-Nitrosodimethylamine (NDMA)	2A		0.0007 ppm; 0.0002 mg m^{-3}					
N-Nitrosodiethylamine (NDEA)	2A		Private 0.0002 ppm; 0.001 mg m^{-3}					
N-Nitrosomorpholine (NMor)	2B		Private 0.0002 ppm; 0.001 mg m^{-3}					
N-Nitrosopiperidine (NPip)	2B		Private 0.0002 ppm; 0.001 mg m^{-3}					
N-Nitrosodiethanolamine (NDELA)	2B		Private 0.0004 ppm; 0.001 mg m^{-3}					
N-Nitrosopiperazine (NPz)	Not rated							
1,4-Dinitrosopiperazine	Not rated							

5. ALTERNATIVE PCC AMINE SYSTEMS AND THEIR EMISSIONS

The best amine unit is the one that demonstrates minimum energy requirement, high degree of CO_2 capture, minimum liquid waste, and minimum amine related emissions to air. Amines represent a health risk, but there is a lack of knowledge on health risks related to amines used for CO_2 capture. The health hazards of amines are strongly dependent on types of amines that are used in the CO_2 capture process and the actual amount of amine emissions. MEA, the most commonly used amine for CO_2, is less toxic and is biodegradable whereas the other amines such as 2-amino-2-methyl-1-propanol (AMP), N-methyl diethanolamine (MDEA) and piperazine (PZ) are ecotoxic and have comparatively low biodegradability[119]. The CO_2 absorption characteristics of MEA are also superior than the other amines[120] but the thermal and oxidative degradation of MEA produces a number of toxic emissions. MDEA/PZ will have a low rate of oxidative degradation and is less volatile than MEA. Piperazine is also resistant to oxidative and thermal degradation and has a lower volatility than MEA. PZ/AMP is resistant to oxidative and thermal degradation and AMP is more volatile. The Cansolv solvent, either diethylenetriamine (DETA), triethylenetetramine (TETA) or tetraethylenepentamine (TEPA) is probably also resistant to oxidative degradation. KS-1 is believed to be resistant to oxidative and thermal degradation and may therefore be a good choice. This section examines two other amine based processes and compares them with the base case, with and without application of emission control methods. It is to be noted that some of the emission control methods suitable for ammonia emission control in MEA based unit could also be used for controlling ammonia emission from the ammonia process.

5.1 Amino Acid Salts

5.1.1 Technology Description

As reported in the literature, the amino acid salt[121] solutions have a relatively fast rate of CO_2 absorption, higher selectivity for CO_2 absorption, higher stability towards oxygen and a more favourable binding energy but have lower CO_2 sorption capacity than MEA solution[122,123]. It is also claimed that many amino-acids are also naturally occurring and have favourable biodegradation properties. Due to these favourable properties, the amino acid salts have been deployed for commercial scale acid gas removal processes in the past, as for example in the Alkazid process by BASF[124]. These favourable properties of amino acid salts appears to make them suitable for membrane contactors which are compact and cost effective[125]. The oxygen resistance of amino-acid salts also seems to make them suitable for CO_2 separation from flue gas[126,127]. The details of these processes could not be found but simulation data reported in the literature[128] refers to a unit capacity of about 3000 tonnes of CO_2 capture per day.

In recent years some other amino acid salts based solvents such as PuraTreat (BASF) have also been developed for the selective removal of H_2S and CO_2 specifically in gas streams containing olefins and oxygen. In addition to high stability in the presence of olefins and oxygen, the use of PuraTreat is claimed to be associated with negligible vapour pressure. The PuraTreat is claimed to be an ethanolamines free solvent and its components are biodegradable. It is claimed that this solvent has been trialled for post-combustion CO_2 capture at power station in Australia to capture up to 50 tonnes of CO_2 per day. Much of the CO_2 captured at this unit is claimed to be used in the neutralisation of ash water, producing calcium carbonate and effectively sequestering the CO_2[129].

Siemens AG has also claimed to have developed a proprietary post-combustion carbon capture technology PostCap^{TM} based on aqueous amino-acid salt solutions (AAS). It is claimed that this solvent has a low absorption enthalpy and near-zero vapour pressure, permitting an economic and environmentally friendly capture process. The capture process has been investigated in Siemens' laboratory unit and with real flue gas in a slip-stream pilot unit at E.ON power station Staudinger, Unit 5 in Germany in the PostCap^{TM} project. The pilot unit is the crucial step on the way to implementation of the aqueous ammonia amino acid salt solutions into demo units. The energy requirement for regeneration of the amino-acid salt solution is reported to be 2.7 GJ/ton CO_2 which compares favourably with the regular amine processes. Solvent stability and low emissions are claimed to be experimentally confirmed by Siemens. The results indicated that the amino-acid salt is stable against thermal conditions and oxygen environments which prevail under real operating conditions. According to Siemens claims, the total loss of solvent per year due to O_2 and thermal degradation can be estimated to be less than 20 % of the amount required in the standard MEA process. Additionally, a proprietary reclaiming process for AAS is under development as reported in the literature. No mentionable amounts of emissions solvent or nitrosamine/nitramine are reported to be found in the CO_2 reduced flue gas of the POSTCAP^{TM} pilot unit[130,65].

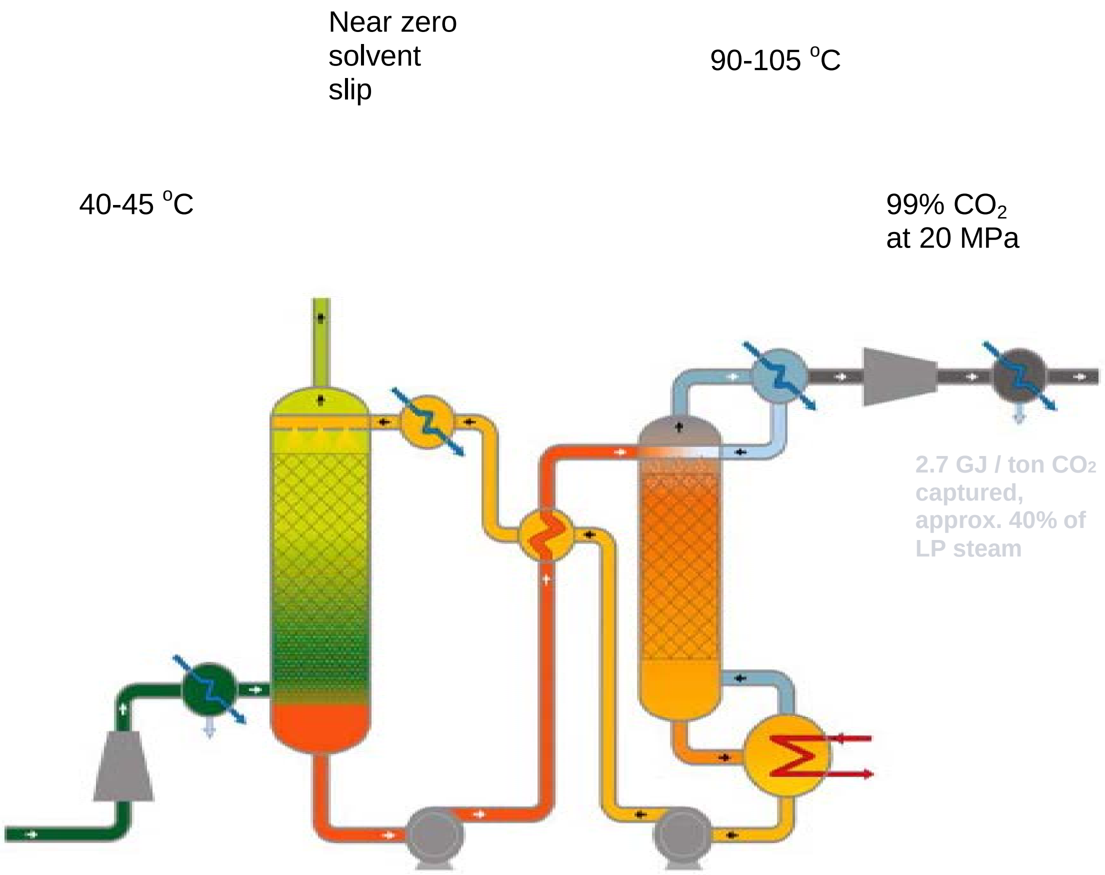


Figure 26 Siemens PostCap^{TM} Amino Acid Salt Process[131]

The basic process flow scheme, as shown in Figure 26, is similar to MEA process but there are advantages of easy handling, low volatility and low degradation of amino acid salt. In addition, the PostCap^{TM} process uses several advanced features in an improved process set-up, which are not shown in Figure 26.

During 2010, Siemens was awarded a US$ 15 million grant from Department of Energy to build its first pilot unit for CO_2 capture project at a coal-fired power plant in the U.S.A. This project aims at demonstrating the new PostCap^{TM} technology, utilising an aqueous amino acid salt solution as a solvent for CO_2 absorption[131]. This pilot unit seems to be aimed at demonstrating the overall performance of the amino acid salts process, particularly the stability of solvent and low emissions with the flue gas.

It is reported that Siemens Energy has a plan to design, install, and operate a pilot unit for treating a slipstream (1 MW equivalent) at the Tampa Electric Big Bend Station to demonstrate POSTCAP technology for post-combustion CO_2 gas capture. The primary goal of this project is claimed to be to reduce the large amounts of energy needed to operate the carbon capture unit. This new carbon capture demonstration is supposed to be installed downstream of the existing Wet FGD system and was aimed to capture 90% of CO_2 from a slip stream of flue gas. As reported the pilot unit is scheduled to be in operation in 2012[131],and it is likely that the realistic performance data of the amino acid salt process will be generated from this pilot unit.

Another advantageous characteristic of amino acid salt is claimed to be the precipitation of either bicarbonate salt or neutral amino-acid when CO_2 loading exceeds a certain value. Due to the precipitation the equilibrium pressure of CO_2 remains constant even when the CO_2 loading of the solvent is further increased. This is because with the increase in CO_2 concentration above a certain value in the salt solution an equilibrium proportion of CO_2 is precipitated either as neutral amino-acid molecule or a bicarbonate salt[127,132] and a constant concentration of CO_2 in salt solution phase is also maintained at equilibrium. As a result the driving force for absorption can be maintained at a high level even at high loadings. It is claimed that this precipitation characteristic significantly improves the absorber performance. Furthermore, the high loadings lead to reduced energy consumption during regeneration. The use of precipitating solvents requires some modifications of the equipment design used in conventional amine process and these modifications may have additional costs. For example, the absorber should be able to handle slurries, and the temperature profile during desorption requires the heat exchanger to be partly integrated into the stripper column. Based on amino acid salt, the patented DECAB process is also currently under development[121] by TNO (Toegepast Natuurwetenschappelijk Onderzoek, Netherlands Organisation for Applied Scientific Research).

5.1.2 Emissions from amino acid salt process and its control

Siemens' amino acid salt based post combustion capture process (PostCap^{TM}) has been tested at pilot scale by Siemens at the Staudinger Power Plant in Germany. Siemens reported that the POSTCAP process has achieved a CO_2 capture efficiency of over 90% with practically zero emissions and loss of the solvent with the flue gas. As reported in the literature, this process does not require any downstream scrubbing of flue gas after CO_2 capture. The solvent also captures a number of contaminants present in the flue gas and form non-volatile byproducts which are reclaimed in an innovative separation process. According to Siemens the salts produced from the interaction with flue gas contaminants and CO_2 are naturally occurring stable compounds which are non-flammable, non-explosive and odorless. There was only 1 ppm ammonia emission reported during 4000 hour operation at Staudinger Power Plant and emissions of volatile organic compounds (VOC), formaldehydes, methylamine and nitrosamines were not detectable[133,65]. However, further results from the long term operation of the unit will be required to confirm the performance, particularly the thermal and oxidative, of the amino acid salt based solvent

5.2 Aqueous or Chilled Ammonia Process (CAP)

5.2.1 Technology Description

Despite the fact that ammonia is toxic and corrosive, considerable attention has been drawn to aqueous ammonia (AA) based processes. As claimed in the literature, the main attraction is ammonia's estimated 3 times more CO_2 uptake capacity[134], relatively higher stability and less corrosive nature as compared to MEA[135]. Moreover the regeneration energy required by ammonia is reported to be about three times less and this is reflected in reduction in capital and operating cost by about 15% and 20%, respectively, as compared to with MEA[136,137]

Ammonia based systems are claimed to be operated effectively at lower temperature which also minimises ammonia volatility and the potential for its slippage into the atmosphere. However at very low temperature below 0 ^{o}C, ammonium bicarbonate is precipitated. Ammonia regeneration takes place at lower temperature therefore a low quality waste heat could be used in the stripper of the ammonia process.

It is reported that the impurities such as SO_x and NO_x do not interfere with the process and the ammonium nitrate and sulphate formed are marketable fertilizers. This ammonia based CO_2 capture could also be carried out along with NO_x and SO_x removal[138].

The CAP involves absorbing carbon dioxide into aqueous ammonia at chilled conditions and is actively researched by Alstom[139]. Carbon dioxide is absorbed by direct contact with an ammoniated solution (ammonia concentration ~28 w %) at temperature below 10-20 ^{o}C and ambient pressure to form ammonium bicarbonate that precipitates as a solid. The captured CO_2 is then released by converting ammonium bicarbonate into ammonium carbonate in a desorber at elevated temperature (above 100 °C) and pressures (20-40 bar, 2-4 MPa). The ammonia present in the residual flue gas is scrubbed in a water wash section and is recycled. The flue gas is discharged to the atmosphere

As shown in Figure 28, in the Chilled Ammonia Process CO_2 from the desulphurised flue gas pre-cooled to about 37 ^{o}C is captured by direct scrubbing with lean ammonium carbonate ($(NH_4)_2CO_3$) solution at temperature below 20 ^{o}C. This CO_2 absorption reaction is usually carried out in a spray tower to allow free flow of precipitated ammonium bicarbonate (NH_4HCO_3).

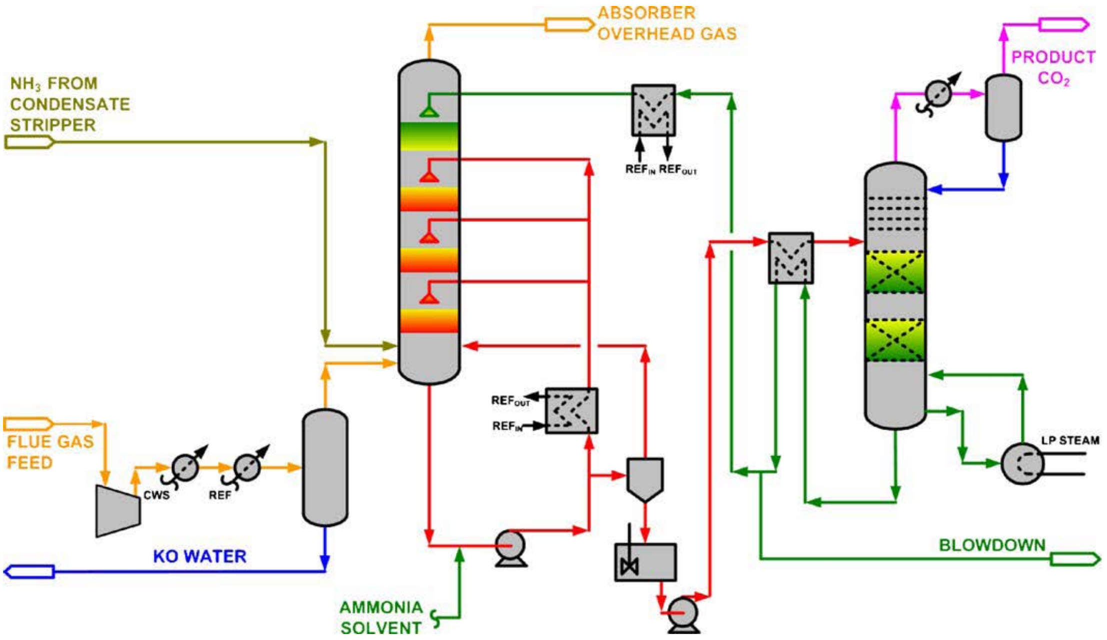


Figure 28 Flow Scheme of Chilled Ammonia Process[134]

The solid is concentrated and sent to the regeneration unit where it is heated to about 80 °C to release CO_2 which pressurises the system. The regenerated lean solution is recycled backed to the absorber and the released CO_2 gas is further processed for storage or consumption in other process. The process demands energy for flue gas precooler, recycle solvent chiller, and absorber chiller. The solvent flow is maintained to absorb about 90% of the CO_2 in flue gas.

A number of pilot and demonstration units seem to have been constructed and operated in the last decade to test the technical and economic feasibility of the ammonia based PCC processes. Alstom and Powerspan are the two major commercial players in this area. Alstom has developed a chilled ammonia process (CAP), in which, as described in the open literature, CO_2 is absorbed in highly ammoniated solution at low temperatures (0-20 °C), producing a slurry containing ammonium bicarbonate. In the stripper, ammonium bicarbonate is converted to ammonium carbonate at temperatures above 100 °C and pressures of 20-40 bar (2-4 MPa). Table 21 summaries the ongoing and planned pilot and demonstration projects of Alstom's chilled aqueous ammonia based capture process.

US based company Powerspan has developed a CO_2 capture process, called ECO2®, in which the absorption takes place at relatively high temperature, above 20 °C, and no slurry is involved in the absorber. Powerspan tested its technology at a pilot unit at FirstEnergy Corp.'s R.E. Burger Plant near Shadyside, Ohio. The 1-MW pilot plant test unit is designed to produce approximately 20 tons of sequestration ready CO_2 per day while achieving a 90 percent capture rate. Commissioning was completed and testing began at the ECO2 pilot facility in December 2008. In May 2010, Powerspan announced results from an independent review of its ECO2® post-combustion carbon dioxide (CO_2) capture technology[140], conducted by an engineering company. The results from 100000 tonne per year capacity validation pilot unit and a 1-1.5 million tonne per year capacity large scale plant will become available by 2013 and 2015, respectively[141].

However, the performance of ammonia process have to be thoroughly evaluated to ascertain the operating costs, energy consumption and emissions prior to any construction of large scale unit is considered. The most likely shortcomings of these processes are likely to be loss of solvent as ammonia and energy required to maintain the solvent at an optimally low operating temperature. The corrosive nature of ammonia and amino acid salt may also require special materials for the construction of the unit at an additional cost as compared to that of MEA unit.

Currently, researchers are actively investigating various techniques for further improving AA and CAP performance, including use of additives that reduce evaporative ammonia losses without sacrificing CO_2 capture performance[142]. The ternary system of NH_3-CO_2-H_2O has liquid and vapour phases and ions from dissociation and precipitating salts. Bai et al[134] showed higher removal efficiencies (>95%) and high absorption capacities (0.9 kg of CO_2/kg NH_3) compared to amine solution. The absorption kinetics of ammonia with carbon dioxide was also reported for the temperatures between 10 and 50 °C. The advantages of CAP are lower heat of absorption of CO_2 compared to the conventional amines, resulting in lower energy requirements, as well as pressurised CO_2 rich product stream, resulting in low energy for compression. The theoretical study conducted by Darde et al[143] compared the CO_2 capture for the aqueous ammonia and aqueous amine solutions. Since ammonia has high volatility, the absorber temperature should be maintained below the room temperature for minimum ammonia loss. According to this study, the operating temperature of the absorber should be at 5 °C and ammonia concentration of 7 w% to avoid precipitation of salts.

Table 21 Summary of the current status of various chilled ammonia based capture projects from

Project title	Location	Customer	CO_2 Source	Capacity (M Tonnes/y)	Commissioning
We Energies Pleasant Prairie Field Pilot	Pleasant Prairie We Energies, USA	We Energies	Pulverised low sulphur sub-bituminous coal fired boiler	15,000	June 2008
E.ON Karlshamn Carbon Capture Field Pilot	Karlshamn, Sweden	E.ON Thermal Power	High-sulphur fuel oil fired boiler	15,000	April 2009
AEP Mountaineer Product Validation Facility	New Haven, West Virginia, USA	American Electric Power (AEP)	Pulverised high-sulphur bituminous coal fired boiler	100,000	September 2009
TCM Mongstad Product Validation Facility	Mongstad, Norway	TCM Company (European CO_2 Technology Center Mongstad)	Residue Catalytic Cracker (RCC) and Natural Gas fired Combined Heat and Power (CHP) Plant	100,000	2011
TransAlta Project Pioneer large scale demonstration	Alberta, Canada	TransAlta	Pulverised low-sulphur, sub-bituminous coal fired boiler	1,000,000	2015

Mathias et al[144] conducted a thermodynamic analysis to evaluate the energy requirements of the chilled ammonia process. The model predicted the refrigeration load (from flue gas chiller, recycle solvent chiller, absorber chiller) has a significant energy penalty and exceeds the benefits of higher pressure CO_2 product from the stripper. The large cost associated with cooling is detrimental to the economic feasibility of the CAP process when compared to the alkanolamine based processes. A study by Darde et al[143] on the CAP predicted a high concentration of ammonia in the gas phase in the absorber, and recommended a suitable cleaning system at the top of the absorber to avoid ammonia loss to atmosphere. The use of aqua ammonia process for simultaneous removal of acidic gases (including CO_2, NO_x and SO_x) has been suggested by Resnik[137]. The other economic reason being the formation of by products mainly ammonium sulphate, ammonium nitrate and ammonium bicarbonate, which are well known fertilisers. The CO_2 removal efficiency of 99% can be achieved with a loading capacity of 1.2 kg CO_2/kg NH_3 compared to 94% and 0.4 kg CO_2/kg NH_3 for MEA, and uses only 50% of the energy required in the conventional MEA process[145].

5.2.2 Emissions from chilled ammonia process and its control

As reported in the literature[138] ammonium carbonate interaction with flue gas impurities and CO_2 in the absorber and its heating in the regenerator does not produce any degradation products. However, some extent of ammonia slippage with the treated flue gas results in emission which is only weakly dependent on the concentration of NH_3 and depends mainly on absorber temperature. At 10 ^oC, the NH_3 slip is approximately 2230 ppmv for 26% ammonium carbonate solution and it could be reduced to 242 ppmv if the absorber temperature is reduced to 0 ^oC, as shown in Figure 29.

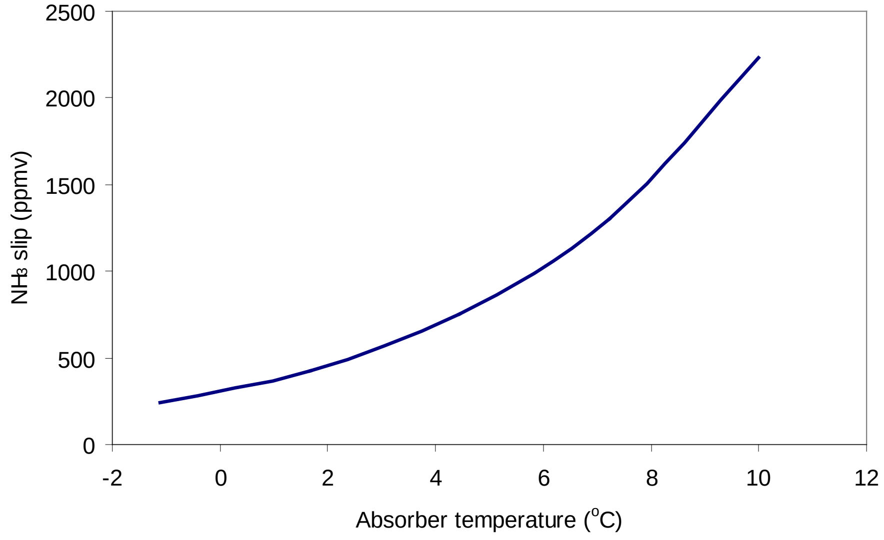


Figure 29 Variation in ammonia emission with absorber temperature.

This means even lower temperature does not completely eliminate ammonia emission and further measures to capture ammonia emission are required. The flow scheme for ammonia emission control strategy is shown in Figure 30, which is essentially water scrubbing.

The chilled ammonia process including water washing or scrubbing has been operated by Alstom Power[146]. This process is expected to have emission of ammonia over 10 ppmv unless an additional method is used to completely eliminate the emission.

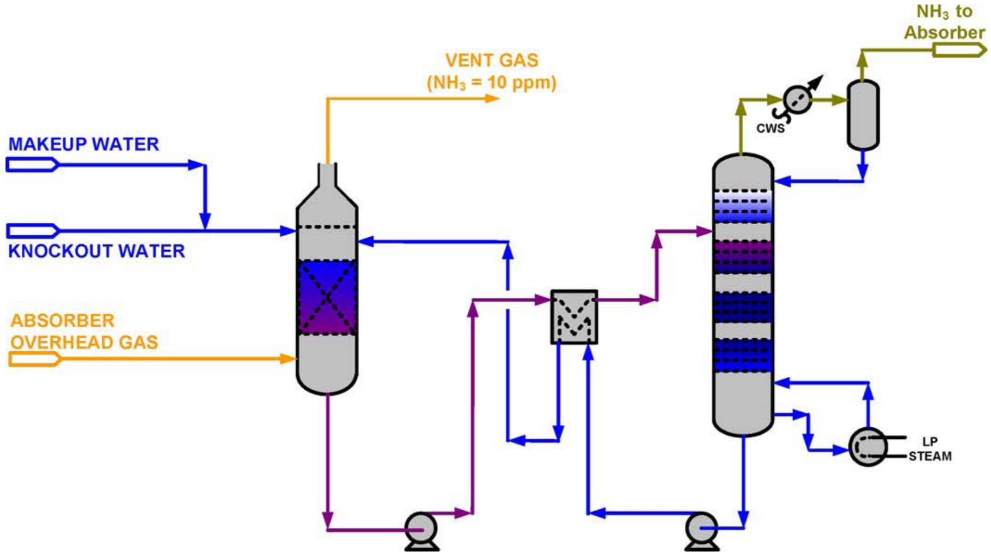


Figure 30 Ammonia emission control strategy for chilled ammonia process[146]

5.3 Application of selected emission control methods

A summary of selected emission capture methods in MEA, amino acid salt and chilled ammonia process is presented in Table 22. Acid scrubbing in the ammonia process will be effective in removing ammonia but this will require further modification of the chilled ammonia flow scheme to prevent contamination of ammonia solvent with acid and include a process to recover and recycle acid and ammonia.

UV treatment will be effective with the acid wash in an amine process but less important for the amino acid salt and aqueous ammonia processes as there is no evidence of nitrosamines formation in their base cases.

Table 22 Comparison of MEA technology with alternate amine technologies with and without emission capture measures

Technology	**Main emissions**	**Anticipated gas emissions (ppmv) from selected methods**				**Comment**
		Base case	**Three water wash**	**Acid wash**	**[2]UV/O_2/ H_2O_2**	
MEA	NH_3	0-10	0-2[41]	0-1[42]	0-1[61,62]	Combined effect of UV and acid wash need to be evaluated
	MEA	10-25	8-11[41]	0[42]	4-10[61,62]	
	Nitrosamine	6-70	-	0[42]	0.7-17[61,62]	
	Other	0-4				Refer Table 13
Amino acid salt	NH_3	1[133]	0.8[41]	0[42]	0.4[61,62]	Acid and salt recycling with acid wash to be evaluated.
Chilled ammonia	NH_3	242[138]	10[1,146]	0[42]	0.4[61,62]	Acid and salt recycling with acid wash to be evaluated.

[1] *Water washing along with lowering of absorber temperature*
[2] *Without acid wash*

6 SUMMARY AND CONCLUSIONS

The objectives of this study were to: (1) evaluate the predominant toxic and hazardous emissions from the MEA based PCC unit, (2) review available processes and methods which could be applied for emission reduction, (3) review of existing allowable emission limits and regulation for various chemicals likely to be emitted, and (4) evaluate alternative PCC amine technologies and their emissions with and without the emission control processes.

According to the literature reviewed, thermal and oxidative degradation of amine results in a number of gas and liquid phase impurities which reduce the CO_2 absorption capacity of the solvent and produces compounds whose emission is hazardous for the environment. These impurities in the vapour or fine droplet form could be emitted in the CO_2-lean flue gas from the top of the absorber and stripper.

ASPEN modeling was used to estimate emissions from MEA based PCC unit connected to a natural gas fired combined or a coal fired power plant, as defined in a previous IEA-GHG study. The simulation results indicate that the heat stable salts, Oxazolidone-2, 1-(2 Hydroxyethyl) imidazolidone-2 (HEIA), N-(2-Hydroxyethyl)-ethylenediamine (HEEDA), N-(2-hydroxyethyl)-diethylenetriamine (Trimer), N-(2-hydroxyethyl)-triethylenetetramine (Polymer), and Cyclic Urea of Trimer are unlikely to be emitted as gas phase though their concentrations may increase with time in the lean MEA solution. However, they may be emitted as droplets, depending on the dynamics within the absorber and effectiveness of the demister system used.

For the case of the coal fired power plant (CFUS) provided with the MEA based carbon dioxide capture unit without any emission control methods, the results from the simulation of the capture unit indicate that the total MEA emissions are likely to be around 0.014 mg/Nm^3 of CO_2 lean flue gas (0.043 ppmw in CO_2 captured).

In the case of the natural gas fired combined cycled (NGCC) plant provided with the MEA based carbon dioxide capture unit without any emission control methods, the results from the simulation of the capture unit indicates that the MEA emission is likely to be around 5.54 mg/Nm^3 of CO_2 lean flue gas (63.8 ppmw).

Relatively larger emission from the natural gas power plant is mainly attributed to the higher degree of volatilisation of the solvent phase due relatively larger flow of flue gas through the absorber

As reported in the literature, the droplet emission could be controlled by a number of demisters or mist eliminators by capturing fine droplets entrained in the gas phase so that they are not re-entrained into the gas phase.

A number of demisters are commercially available and the review of the performance data indicates that the Swirl Mist Eliminator (SME), which works on the principle of impingement achieved with cyclonic swirling of the fluid, offers a better separation of fine droplets at significantly lower pressure drop than the other demisters. Brownian and wire mesh demisters can also give good separation efficiency but they are susceptible to saturation and Brownian demister offers a higher pressure drop. The SME offers drainage channels isolated from main stream flow to some extent eliminate the possibility of saturation.

The emission of vapours could be captured by (1) single and multiple stage water washing of CO_2-lean flue gas, (2) washing of the flue gas with acid, (3) cooling of the flue gas to condense vapour, and (4) adsorption on to a solid surface.

The concentration of amine in the exhaust of CO_2-lean gas could be brought down from 25 ppm for single washing stage to around 8 ppm for three washing stages. As mentioned earlier the simulation of PCC unit with single stage washing shows about 44 ppm emission of amine. The difference in the emission levels are perhaps due to difference in the conditions of operations used in the simulation and literature.

The use of chilled water scrubbing is effective only for condensable and water soluble components in the vapour but not effective for gases which could not be dissolved or condensed by the scrubbing media. Also cooling reduces the exhaust gas buoyancy

Scrubbing with acid is seen to be proven and currently state-of-the-art and is being used in some of the large scale units. The scrubbing units could also be easily retrofitted into the existing PCC units with the installation of a separate scrubber unit.

Scrubbing with acidic media (H_2SO_4 in water, CO_2 in water, or other dilute organic acids) is more effective because weak bases such as MEA vapour, nitrosamines, aldehydes and ammonia (the main degradation product) are quite soluble in acidic media. This essentially means a possibility of smaller size scrubbers with lower scrubbing media flow rates and corresponding lowering of capital and operating costs as compared to chilled water scrubbing.

With single stage washing with cooled water the MEA concentration in the flue could be reduced from 55-100 ppm down to 0.7 ppm with the ammonia and N-nitrosomorpholin concentration of about 30 ppm (wet) and 0.4 $\mu g/Nm^3$, respectively, in the washed gas. With addition of sulphuric acid to the wash water to enable washing at $pH = 6$, the MEA, ammonia and N-nitrosomorpholine concentrations could be brought down to <0.05 ppm, <1ppm and <detection limit, respectively

Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA) or Pressure Vacuum Swing Adsorption (PVSA) could be used to capture all gaseous degradation products. There is no reference about capturing emissions from the MEA unit, but separation of polar as well as non-polar compounds has been subject of research for the last three decades and there is potential for developing a process optimized for deep cleaning of treated flue gases from MEA unit. Since CO2-lean gas is saturated with water the adsorbers for the unit will have to be provided with appropriate regenerable dehumidification zone to prevent water poisoning of the adsorbents for gases. If more gaseous products have to be separated a multi zoned adsorber with different adsorbents may have to be optimized for this separation.

Emissions of nitrosamines, which in this study were modelled by the compound dimethyl-nitrosamine ($C_2H_6N_2O$), were shown to be amenable to acid wash and UV degradation.

The emissions from two alternate amine technologies have also been reviewed and compared with the MEA process. The amino acid salt and chilled ammonia processes are seem to be promising as it is claimed in the literature that these processes do not have any issue of degradation of solvent and emissions. There are initial indications that these processes have significantly less emissions as compared to MEA process. However, further evaluation of these processes and their emissions at laboratory and pilot scales will be desired prior to the development of a commercial scale unit.

The chilled ammonia (CA) or aqueous ammonia (AA) process does not have any reported degradation products and their base case emission of ammonia is reported to be below 1 and 10 ppmw, respectively. On application of acid wash the emissions from these processes could be brought down to zero. UV, plasma and other oxidative methods may not be necessary for these processes as there is no report on nitrosamine emissions from these processes. However, acid treatment process, recirculation or disposal of acid and salt have to be further studied in the laboratory prior to implementation at larger scale. Because of process stability, high rate of CO_2 sorption and loading, negligible degradation and emissions, the alternative technologies seems to have great potential for future applications

Current air quality guidelines have been also reviewed to evaluate the likely environmental impact of all the emissions from PCC units.

Current air quality guidelines do not apply specifically to the materials likely to be present in amine-based PCC emissions which, nevertheless, will probably be subject to these guidelines indirectly. Ammonia, which is likely to be a major component of emissions from these units, is already subject to European legislation designed to limit emissions from member states. Large-scale deployment of amine systems has the potential to affect the ammonia budgets of individual countries and consequently ammonia emissions will be subject to public scrutiny. As well as ammonia, many of the expected atmospheric emissions from amine PCC units will contain nitrogen and these too, may be of significant concern because of their potential to contribute to the overall nitrogen load within the environment. Hence these materials may be indirectly regulated by current legislation that limits nitrogen deposition in the environment. Some of the volatile compounds that may be emitted may also contribute to the formation of ozone and particulates, both of which are regulated criteria pollutants.

Transboundary transport of pollutants is a continuing problem in Europe and elsewhere, and with large scale deployment of amine PCC systems, emissions will have to be considered not only within the national context, but also on how they will affect neighbouring countries. Current European Union policy aimed at significantly reducing air pollution, including emissions of ammonia, is likely to affect requirements relating to PCC units.

At a more local level, without effective additional treatment there could be numerous amine and related products in the air within and surrounding the unit. Some of these compounds are already recognised as industrial pollutants with adverse health effects and occupational exposure limits have been set to protect workers in industry. Many of the compounds considered in this study as potential PCC emissions are covered by existing occupational exposure limits currently in place in various countries. However, nitrosamines, which are particularly toxic and probable carcinogens, are not well covered by suitable exposure limits. Formaldehyde is also a known carcinogen and although some OELs are legislated in various countries, it is currently thought that there is no safe exposure limit value.

In the short term, it is likely that these existing regulations can be adopted for PCC installations. However further work will be required to ensure that appropriate controls are in place to protect workers and the general population from the effects of materials that do not have appropriate health-based exposure limits. In addition, the effect of many of these materials on the environment is not fully understood and will be an area of active research.

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