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Dossier

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PART 1

Post Combustion CO_2 Capture
Captage de CO_2 en postcombustion

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Dossier

Post Combustion CO_2 Capture
Captage de CO_2 en postcombustion

Emissions to the Atmosphere from Amine-Based Post Combustion CO_2 Capture Plant – Regulatory Aspects

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Résumé — Émissions atmosphériques des installations de captage de CO_2 en postcombustion par les amines – Aspects réglementaires — Le captage en postcombustion (PCC, *Post Combustion Capture*) du CO_2 par les amines est une technologie immédiatement disponible à même d'être déployée pour réduire les émissions de CO_2 des centrales électriques au charbon. Cependant, il est probable que les installations de PCC rejetteront de faibles quantités d'amines et de produits de dégradation des amines dans les gaz de fumées traités. Les effets environnementaux potentiels de ces émissions ont été examinés dans diverses études partout dans le monde. En se basant sur les gaz de fumées d'une centrale électrique au charbon ultra-supercritique de 400 MW, des simulations avec Aspen-Plus du procédé PCC ont été utilisées pour prédire les émissions atmosphériques potentielles de la centrale. De nouvelles données issues de divers projets de recherche menés dans ce domaine ont réduit significativement la perception du risque de rejet d'amines et de produits de dégradation d'amines dans l'atmosphère. En plus de la réduction des émissions de CO_2, la technologie PCC est aussi à même d'assister la réduction des émissions de SO_x et de NO_2. Cependant, certains autres polluants, tels que NH_3 et les aérosols, risquent de voir leurs émissions augmenter si des technologies de contrôle appropriées ne sont pas adoptées. Pour étudier la photo-oxydation atmosphérique des amines, des tentatives de développement de modèles des réactions chimiques permettant l'évaluation de la qualité de l'air ont été effectuées. Cependant, une recherche plus approfondie dans ce domaine reste nécessaire pour estimer la réactivité des solvants aminés en présence d'autres polluants tels que les NO_x et les autres composés organiques volatiles présents dans l'air.

Les directives de qualité de l'air existantes devront peut-être être mises à jour afin d'inclure les limites des autres polluants tels que NH_3, les nitrosamines et les nitramines, lorsque plus d'information sur leurs émissions devient disponible. En termes de directives de qualité de l'air et autres aspects réglementaires, cet article se focalise sur la description des prédictions des concentrations des principaux polluants potentiellement rejetés par une centrale au charbon, prédictions obtenues par des simulations de procédé ASPEN-Plus PCC.

Abstract* — *Emissions to the Atmosphere from Amine-Based Post Combustion CO_2 Capture Plant – Regulatory Aspects — *Amine-based Post Combustion Capture (PCC) of CO_2 is a readily available technology that can be deployed to reduce CO_2 emissions from coal fired power plants. However, PCC plants will likely release small quantities of amine and amine degradation products to the* *atmosphere along with the treated flue gas. The possible environmental effects of these emissions have been examined through different studies carried out around the world. Based on flue gas from a 400 MW ultra-supercritical coal fired power plant Aspen-Plus PCC process simulations were used to predict the potential atmospheric emissions from the plant. Different research initiatives carried out in this area have produced new knowledge that has significantly reduced the risk perception for the release of amine and amine degradation products to the atmosphere.*

In addition to the reduction of the CO_2 *emissions, the PCC technology will also help in reducing* SO_x *and* NO_2 *emissions. However, some other pollutants such as* NH_3 *and aerosols will increase if appropriate control technologies are not adopted. To study the atmospheric photo-oxidation of amines, attempts are being made to develop chemical reaction schemes that can be used for air quality assessment. However, more research is still required in this area to estimate the reactivity of amino solvents in the presence of other pollutants such as* NO_x *and other volatile organic compounds in the background air.*

Current air quality guidelines may need to be updated to include limits for the additional pollutants such as NH_3*, nitrosamines and nitramines once more information related to their emissions is available. This paper focuses on describing the predicted concentrations of major pollutants that are expected to be released from a coal fired power plant obtained by ASPEN-Plus PCC process simulations in terms of current air quality regulations and other regulatory aspects.*

INTRODUCTION

The world's dependency on coal and gas for its major share of energy demand requires the development of a comprehensive approach for capturing and storing CO_2 emissions produced during the combustion of these energy sources (IPCC, 2005). It is likely that some expected greenhouse gas reduction programs are being delayed until a carbon technology can be developed and deployed. Currently carbon tax are being introduced in different countries around the world including Australia and new performance standards limiting carbon dioxide emissions from power plants are being planned or introduced (European Commission, 2013). On March 27, 2012, the USEPA (United States Environmental Protection Agency) announced new standards that limit CO_2 emissions to 1 000 lb per megawatt-hour (454 kg MWh^{-1}) (USEPA, 2012). This means that all new coal-fired power plants may be required to adopt new technologies to capture or reduce their anticipated emissions. Therefore, any proposed carbon capture technology should be developed in concert with any emerging environmental regulations.

Carbon Capture and Sequestration (CCS), has been widely recognised as a technology that can be used to mitigate the CO_2 emissions from power plants and from other energy intensive facilities. The technology is based on separating the CO_2 from a selected flue gas to produce a pure CO_2 stream that can be captured. The captured pure CO_2 will be compressed to a dense fluid that can be transported and injected in the underground for long term storage. Currently, the most effective and available technology for CO_2 capture from the flue gas of power plants is based on the chemical interaction between the flue gas and selected organic solvents occurring in an absorber/stripper system that can selectively absorbs then releases CO_2.

A typical 400 MW pulverised coal fired power plant produces about 1 000 000 m^3 of flue gas per hour, containing CO_2, H_2O, N_2, O_2, NO_x, SO_x and fly ash. The large quantities of gases that must be managed to carry out efficient CO_2 capture presents a technical and scientific challenge for the following several reasons:

- the high volume of gas to be treated (for a 400 MW plant around 5 000 t of CO_2 per day should be treated);
- the flue gas is at atmospheric pressure and the CO_2 is diluted (under 15% CO_2);
- the flue gas contains other trace impurities and oxygen that will affect the separation efficiency.

Amine-based Post Combustion CO_2 Capture (PCC) technology that is commercially available although it has not been tested at full scale power generation plants (GCCSI, 2012). Nevertheless, PCC shows promise as a near-term solution to capture CO_2 from flue gas of fossil fuelled power plants. This technology can be easily deployed and retrofitted to the existing fossil-fuelled power plants. Amine solvents can degrade under the interactions with different compounds existing in the flue gas and under different plant operational conditions to produce different degradation products. While the most widely used and discussed solvent is the aqueous solution of 0.3 g/g MonoEthanolAmine (MEA), different solvents are being synthetised and tested in the aim to improve the overall properties and performance of CO_2 capture.

A number of PCC pilot plants from around the world using MEA (Moser *et al.*, 2011; Knudsen *et al.*, 2011; Strazisar *et al.*, 2003) have reported the presence of different degradation products at different sections of the plant, resulting from the interaction between the flue gas constituents and the amines. These products reduce the efficiency of the solvent and create a challenge for the management of wastes materials. Some of these products have the potential to be directly released from the plant as gaseous compounds while others may be entrained in droplets to reach the atmosphere. In the atmosphere, amines and their degradation products can undergo further chemical reactions to produce new products, some of which may be toxic (IEAGHG, 2012; Karl *et al.*, 2012; Pitts *et al.*, 1978; Grosjean, 1991). For amine-based PCC plants, therefore, the identification and quantification of major degradation products of health and environmental concern are required. The degradation compounds will be reported to regulatory agencies to assess the environmental impacts of the plant emissions. It is important that any potential risks associated with these releases are identified and mitigated before PCC systems are deployed for capturing CO_2 from coal fired power plant flue gas.

The assessment of the potential health and environmental impacts of amines and amine degradation products being released to the atmosphere from PCC plants has lately attracted a lot of research around the world (Koornneef *et al.*, 2012; Brakstad *et al.*, 2010; Thitakamol *et al.*, 2007). This research is intended to reduce gaps in the current knowledge and to provide a better understanding of the various issues related to the atmospheric fate of amine release to the atmosphere. In the current paper, the use of MEA to scrub the CO_2 from a coal-fired power plant forms the focus of the following discussion. Results and analysis of major degradation products will be discussed. This paper focuses on application of process simulation towards predicting the atmospheric emissions from an amino solvent based post combustion capture plant.

1 MAIN DEGRADATION PRODUCTS

The amine used to capture CO_2 has the potential to degrade in the process and in the atmosphere after being released from the plant. Solvent will degrade in the process under the influence of the plant operating conditions and by interaction with the flue gas chemical contents and in the atmosphere by interacting with the background air chemical species.

Despite considerable efforts to understand the amine degradation pathways occurring in the process, there are still many gaps in the knowledge. Solvent degradation is a challenging issue that affects the performance the CO_2 capture of amine-based PCC system and may also increase corrosion rates which reduce equipment life (Reynolds *et al.*, 2012; Gouedard *et al.*, 2012; Lepaumier *et al.*, 2011). For MonoEthanolAmine (MEA), a common and widely studied amine solvent, two recognised degradation pathways are:

- oxidative degradation driven by oxygen and other constituents in the flue gas entering the absorber (Bedell, 2009; Goff, 2005; Sexton and Rochelle, 2006),
- thermal degradation driven by high temperatures in the process (Davis, 2009; Thitakamol *et al.*, 2007).

Oxidative degradation takes mainly place in the absorber while the thermal degradation occurs mainly in the stripper process. The solvent degradation is responsible of the production of many intermediate and final species in the process. The volatility of these compounds can be used to predict the most likely compounds that are likely to leave the plant to the atmosphere. Volatile (and some less volatile species) may be emitted at different concentrations to the atmosphere while others can accumulate in the liquid and solid waste in the reclaimer. The accumulation of non-volatile contaminants in amine solutions may also create undesirable operational problems.

It has long been recognised that CO_2, O_2, SO_x, NO_x and other compounds in flue gas from coal fired power plants undergo complex chemical reactions with MEA to produce different degradation products. The presence of selected trace metals such as Fe and Cu was found to catalyse these paths (Goff and Rochelle, 2004; Sexton and Rochelle, 2009). Ammonia, aldehydes, amides and hydroxyacetaldehyde were recognised as primary products resulting from this degradation (Sexton and Rochelle, 2011; Chi and Rochelle, 2002). Reactions between aldehydes and oxygen produce carboxylic acids that may dissociate in the solution to form heat stable salts. In addition, ammonia formed by solvent degradation reacts with MEA in the presence of oxygen to form amides and alkylamines.

Because of the complexity involved in describing the appropriate chemical reaction pathways of the solvent degradation, different degradation mechanisms have been proposed but these mechanisms are still far from being complete (Angove *et al.*, 2011a, 2011b). As a result of the complexity of properly describing the chemistry of amine degradation, the appropriateness of process modeling results would depend on the accuracy of the adopted chemical reaction scheme.

Nitrosamines and nitramines were reported as possible degradation products resulting from the interaction between organic amines and nitrosating agents such as nitrate and nitrite (Masuda *et al.*, 2000; Attalla and Azzi, 2009, 2010; Brakstad *et al.*, 2010; Pedersen *et al.*, 2010).

Sun *et al.* (2011) reported that carbonyl compounds formed by oxidative degradation of amine have the potential to catalyse the nitrosation of amines. These compounds are of major concerns because their potential risks on human health. However, it is unclear how much of these substances will be formed and emitted during the capture process or formed in the atmosphere after emission. It is known that in the atmosphere and under the influence of sunlight nitrosamines can be readily photolysed while nitramines have longer lifetimes. More research is needed for the identification and quantification of nitrosamines and nitramines.

In summary, despite the substantial progress achieved lately in identifying the generation of by-products in the process, there are still many uncertainties that need to be properly addressed.

Amines and their degradation products that leave the PCC plant to the atmosphere will undergo chemical and physical transformation in the atmosphere. Chemical transformations will be driven by complex atmospheric chemical reactions while the meteorological conditions will control the transport and dispersion of these pollutants (Angove *et al.*, 2012; Attalla and Azzi, 2009). Additional degradation products could be generated depending on their interactions with the surrounding ambient air chemical compounds. The non-linear chemistry of the process of the secondary pollutants formation makes it hard to establish linear relationships to predict these anticipated species and their concentrations. It has been reported that NH_3, aldehydes, amides and particles are produced during the atmospheric photo-oxidation of amines (Angove *et al.*, 2012; Karl *et al.*, 2012).

To study the atmospheric degradation of MEA and other amine solvents, the CSIRO smog chamber has been used to carry out experiments at different conditions to develop the database needed to elucidate the major degradation pathways for amines. The smog chamber data are used to develop and validate chemical mechanisms that can be embedded in air quality models to determine the ground level concentrations of pollutants of concerns. Air quality modeling results can be communicated to stakeholders and regulators to show the environmental performance of the plant. Figure 1 shows an example of the smog chamber results (Angove *et al.*, 2012). In this example, NH_3 and O_3 concentrations are seen to increase as a function of time due to photo-oxidation of MEA in the presence of NO_x.

2 IDENTIFICATION OF EMISSIONS FROM THE PLANT

The current assessment was based on the results obtained using ASPEN-Plus PCC process simulations to determine potential emissions of MEA and its degradation products in the treated flue gas of an MEA-based CO_2 capture plant attached at the end of a 400 MW ultra-supercritical coal fired power plant (IEAGHG – report 2012/07). The PCC plant was assumed to use 30% w/w aqueous MEA solvent at the operating conditions specified in Table 1 (Do *et al.*, 2012).

The process flow sheet developed by *Fluor Daniel Ltd* and given in the IEA GHG PH4/33 report that represents the industrial process concept based on the

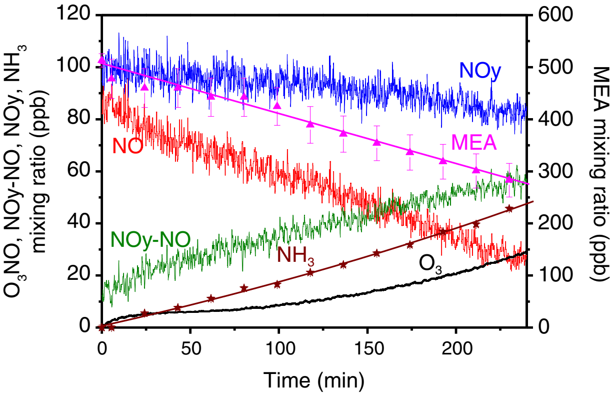

Figure 1

Smog chamber results of an MEA photo-oxidation experiment showing the formation of selected degradation products (Angove *et al.*, 2012).

TABLE 1

Feed flue gas data of the selected ultra supercritical coal-fired power plant used for the simulation (IEAGHG - Report 2012/07)

	Ultra-supercritical coal fired power plant
Flow rate (tonnes/h)	2 973
Temperature (°C)	50
Pressure (kPa)	102.3
Composition	
O_2 (mole %)	4.3
CO_2 (mole %)	12.4
H_2O (mole %)	12.2
N_2 (mole %)	71.1
SO_2 (mg/m^3)	10
NO_x (mg/m^3)	200

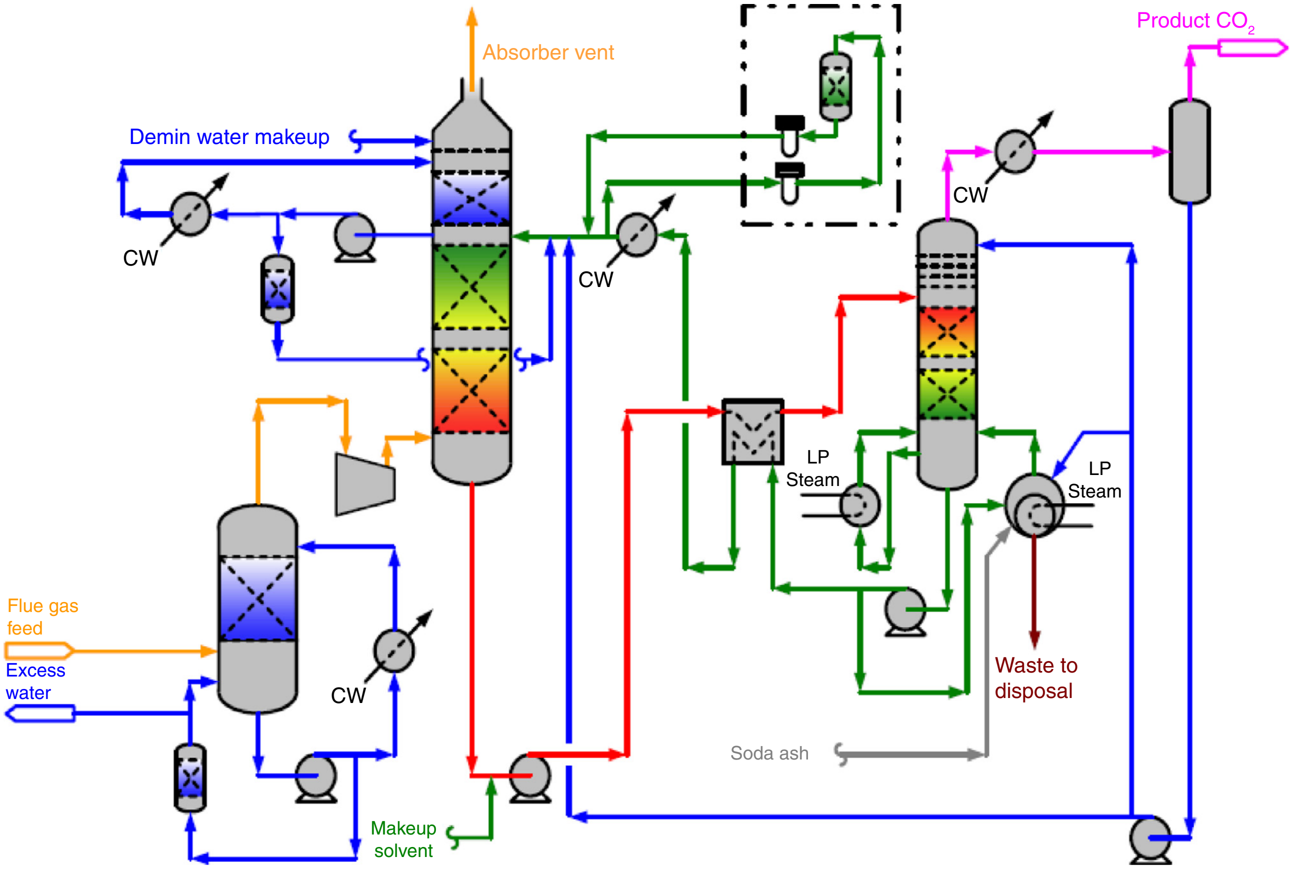

Figure 2

Standard amine-based PCC process flow sheet (Fluor, 2004).

standard amine-based PCC process was adopted for the reported ASPEN-Plus PCC process simulations given in "IEAGHG - report 2012/07". Figure 2 shows a generic process flow sheet that explains the industrial CO_2 capture process concept narrated in the same IEA report.

The CO_2 capture system consists of three main elements: a Direct Contact Cooler (DCC), where the flue gas is conditioned and prepared for the absorption process; an absorber, where CO_2 is absorbed into the amine-based solvent through a chemical reaction; and a regenerator (or stripper), where the concentrated CO_2 is released and the original solvent is recovered and recycled back through the process.

The flue gas is first cooled in the DCC then contacts a circulating sodium hydroxide (NaOH) scrubbing solution to remove up to 98% of SO_2. Removal of SO_2 would minimize the build-up of heat-stable salts in the downstream absorber-regenerator loop.

In the CO_2 stripping section, the CO_2 is liberated from the solvent using steam, producing a low pressure CO_2 product stream and regenerating the solvent for CO_2 capture use. The CO_2 rich solvent leaves the bottom of the absorber and is pumped to the solvent regeneration section of the plant. This is the section where the weakly bonded compound is broken down with the application of heat to liberate the CO_2 and leave reusable solvent behind. The rich solvent from the absorber is first heated in a heat exchanger and then enters the stripper where the rich solvent flows down the stripper through the packed beds counter current to the stripping steam which removes the CO_2 from the rich solvent. The solvent collects on the bottom chimney tray and is sent to the reboiler where low-pressure steam, which is extracted from the cogeneration plant, is used to heat the loaded solvent. The resulting vapor at the top of the stripper contains CO_2 saturated with water. In the stripper, the CO_2 is separated from most of the moisture, yielding a rich CO_2 stream that is sent to the CO_2 product compressor. The lean solvent (*i.e.*, with CO_2 removed) is routed back to the absorber *via* the rich/lean heat exchanger.

A slipstream of the lean solvent is periodically treated in a solvent reclaiming section to remove contaminant by-products that can gradually build up in the circulation loop. Oxidative degradation and the presence of acid gas impurities in the flue gas lead to the formation of heat-stable salts in the sorbent stream, which cannot be dissociated even on application of heat. To avoid accumulation of these salts in the solvent stream and to recover some of this lost solvent, a slip stream of hot lean solvent from the bottom of the stripper is removed through a semi-continuous reclaiming operation and sent for proper disposal. The rate at which this reclaimer effluent waste stream is generated varies according to the capacity and running conditions of the CO_2 capture system. The reclaimer effluent comprises heat-stable salts, non-volatile solvent degradation products, and unrecovered solvent. Typical disposal measures for this type of waste are incineration and landfilling.

The SO_2 concentration in the feed flue gas from the selected power plant was set at 10 mg/m^3 in accordance with the flue gas desulphurisation plant operation upstream and 95% of 200 mg/m^3 concentration of NO_x in the flue gas was considered to be NO with rest being NO_2.

The CO_2 capture plant releases the CO_2 lean stream to the atmosphere from the top of the absorber. During the process, chemical compounds are produced as a result of complex chemical reactions occurring in the absorber. Some of these products continue to recycle in the plant while others such as amines, ammonia, aldehydes, carboxylic acid etc. may be released to the atmosphere.

The bulk composition of the treated flue gas would differ from the incoming flue gas primarily in CO_2 and water. Furthermore, the CO_2 capture system would perform trim SO_2 removal and would also remove some ammonia, HCl, and HF, plus part of the particulates and a portion of the NO_x. The incoming flue gas contains NO_x as nitrogen oxide (NO) and nitrogen dioxide (NO_2). The majority of the NO would pass directly through the CO_2 capture system.

Approximately 95% of the NO_2 would be absorbed either in the DCC or in the CO_2 capture system. The CO_2 capture system would not generate additional NO_x components. The CO_2 capture system would add trace amounts of solvent, ammonia, and other VOC into the flue gas. The incoming flue gas contains SO_x as SO_2 and sulfur trioxide (SO_3). As a result of the pre-treatment and further removal in the CO_2 absorber, the vent gas would be effectively free of SO_2. All of the incoming SO_3 present as very fine mist would be emitted with the CO_2 capture system vent. The CO_2 capture system would not generate hydrocarbons or CO. Any hydrocarbons or CO present in the incoming flue gas would be vented out through the CO_2 capture system stack.

The operating conditions of the absorber top control the amount of the concentrated vapour that is expected to be emitted to the atmosphere. MEA and its degradation products may be released to the atmosphere in accordance with to the vapour pressures of the gas constituents which are dependent on the absorber temperature and concentrations in the solvent. For the considered case study, the used demineralised process water and cooling water inlet temperature were set at 12°C and the maximum rise in cooling water temperature was restricted to 7°C.

The concentrations of MEA and its degradation products obtained in the CO_2 lean gas stream represent the theoretical vapour phase emissions of these chemicals in the treated flue gas and not the physical liquid entrainment based emissions at the plant operating condition. For the purposes of this paper, the highest value of 0.13 m^3 per million m^3 in the range given in the Handbook of Gas Processors Suppliers' Association (2004) was used to estimate physical carryover of wash water in the treated gas that leaves the wash section. From the 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 process simulation assumed CO_2 absorber to have 32 theoretical stages whereas the solvent regenerator (stripper) was assumed to have 38 theoretical stages. The high number of stages was 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 practical purposes the columns should be further optimised. Both the absorber and the stripper were assumed to operate according to chemical rate kinetics with mass transfer considerations (ASPEN Rate-Sep Models). The water wash tower (after the absorber) was assumed to have three theoretical stages and the flue gas temperature at the outlet of the wash tower was set at 45°C. The electrolyte 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 major pathways leading to solvent loss during the CO_2 absorption process are linked to:

- physical liquid entrainment in the treated gas,
- vapour phase carryover in the treated gas,
- solution degradation,
- mist formation produced by nucleation of SO_3 present in the incoming flue gas.

2.1 Simulation Results

During normal operation, the CO_2 capture system vent would emit the treated flue gas. The bulk composition of the treated flue gas would differ from the incoming flue gas primarily in reduced CO_2 and water emissions. Furthermore, the CO_2 capture system would perform trim SO_2 removal, as discussed above, and would also remove some ammonia, HCl, and HF, plus part of the particulates and a portion of the NO_x. The incoming flue gas contains NO_x as nitrogen oxide (NO) and nitrogen dioxide (NO_2). The majority of the NO would pass directly through the CO_2 capture system. Approximately 95% of the NO_2 would be absorbed either in the DCC or in the CO_2 capture system. The CO_2 capture system would not generate additional NO_x components. The CO_2 capture system would add trace amounts of solvent, ammonia, and other VOC into the flue gas.

The incoming flue gas contains SO_x as SO_2 and sulfur trioxide (SO_3). Over 98% of the incoming SO_2 would be removed in the DCC. The remaining SO_2 in the flue gas would react with the amine-based solvent in the CO_2 capture system; therefore, the vent gas would be effectively free of SO_2. However, for achieving improved solvent performance, it is recommended to reduce SO_3 below 10 mg/m^3 before entering the absorber. SO_3 contributes to solvent losses due to the potential formation of aerosols that would be emitted with the CO_2 capture system vent. The CO_2 capture system would not generate hydrocarbons or CO. Any hydrocarbons or CO present in the incoming flue gas would be vented out through the CO_2 capture system stack.

The CO_2 capture system was designed to achieve a 90% CO_2 capture efficiency during steady-state operations. While the CO_2 capture system may offer the additional benefit of reducing some other residual emissions as described above, these other reductions would be ancillary benefits and not the focus of the CO_2 capture process.

With the exception of VOC emissions (*i.e.*, amine solvent and acetaldehyde, as discussed below), the CO_2 capture system is not expected to increase the emission rates of any regulated emissions in the flue gas stream exiting the facility.

The chemical reactions used in the current simulations were based on information available in the open literature. However, because of the gaps in the available information not all reactions could be modelled and not all compounds were available in the Aspen-Plus database. To overcome these difficulties, we have utilised the following power-law kinetic model developed by Uyanga and Idem (2007) to predict the rate of MEA degradation:

$$-R_{MEA} = 0.00745^{*}\mathrm{e}^{-45258/RT}{}^{*}[\mathrm{MEA}]^{1.9}{}^{*}[\mathrm{CO_2}]^{-0.3}\{[\mathrm{SO_2}]^{3.4} + [\mathrm{O_2}]^{2.8}\}$$

where, $-R_{\mathrm{MEA}}$ is the rate of O_2- and SO_2-induced degradation of MEA (mol/(L.h)) and R the gas constant (8.314 J/(mol.K)). [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).

The simulation results show that NH_3, aldehydes, amides will be emitted from the plant at different rates. However, the three principle heavier degradation products oxazolidone and other low volatility products shown in Table 2 were found to have extremely low emission levels in the current simulation. The selected single stage water wash appeared to be very effective in removing these low volatility compounds. In addition, carboxylic acids (HCOOH) that are produced during the

TABLE 2

Likely maximum atmospheric emissions of MEA and its degradation products from the water wash tower (IEAGHG, 2012)

Emissions	Total (mg/Nm^3(dry))
MEA	1.38E-02
Ammonia	1.14E+00
DEA	4.43E-05
Formaldehyde	2.99E-01
Acetaldehyde	3.16E-01
Acetone	3.84E-01
Methylamine	2.44E-01
Acetamide	1.94E-04
HEEDA	6.72E-13
Oxazolidone	1.55E-09
HEIA	2.98E-12
Trimer	0.00E+00
Cyclic urea	0.00E+00
Polymer	0.00E+00

degradation of MEA are trapped as stable salts in the solvent.

Emissions of SO_2 from the flue gas slipstream would be effectively eliminated and emissions of HCl, HF would be substantially reduced when the capture system is operational. Emissions of amine solvent NH_3, and acetaldehyde, which may be formed by reaction of the amine-based solvent with oxygen present in the flue gas, would be increased.

As mentioned earlier, it has been recognised that the use of amine-based solvents to capture CO_2 may result in emissions of a group of nitrosamines and nitramines that are potentially harmful for human health and the environment. These substances that are formed in the PCC process during interactions between the amines and selected flue gas constituents may exist at extremely low concentration levels. It is anticipated that small amounts of these compounds may be emitted with the treated flue gas to air or captured in other waste streams. The exact reaction mechanisms describing the formation of these substances are very complex and more knowledge is needed before proceeding with any predictions of these substances. The modeling results of nitrosamines and nitramines were not included in the present paper.

Table 2 summarizes the estimated concentrations of the treated flue gas exiting the CO_2 capture facility. It shows the likely atmospheric emission compounds and their calculated concentrations in the vapour and droplet phases for the selected case study of a post combustion CO_2 capture plant that processes coal-fired power plant flue gas using 30% w/w aqueous MEA solution. The shaded section of Table 2 highlights the predicted extremely low concentration values of some of these compounds.

The list of the identified compounds that are expected to be released from a PCC plant includes reactive species that are likely to affect the levels of air pollution present over downwind areas depending on the type of the prevailing ambient conditions. Each of these compounds would generate different types of pollution ranging from the production of ozone, NH_3, aerosols, NO_2, etc. Amines degradation in the atmosphere has attracted a lot of attention where different research programs were initiated to improve our understanding on the topic.

3 EMISSION STANDARDS AND LEGISLATION

Emissions from amine-based PCC plant would be examined in terms of their types and amounts. The ambient concentration of each pollutant is determined by the amount of emissions released from the plant and the prevailing meteorological conditions that are able to transport and dilute such emissions. Analysis of potential short-term and long-term air quality impacts of the proposed plant and the use of applicable regulations are the basis for qualifying future operation of a PCC plant. Mitigation measures will be recommended, as necessary, to reduce significant air quality impacts.

Environmental setting and environmental impacts could be used to assess emissions from an industrial plant:

- environmental setting consists of the description of existing regional and local environmental conditions relevant to the plant location;
- environmental impacts describe the significance of the anticipated pollutant emissions relatively to the existing environmental thresholds above which the anticipated emissions would have significant effects on the environment.

Regulatory agencies specify maximum acceptable levels of air pollutants for a selected region. Emissions of carbon monoxide (CO), NO_x, SO_2, Hydrogen Fluoride (HF), Hydrogen Chloride (HCl), and Particulate Matter (PM) from the flue gas are currently authorized under existing air permits issued by regulators. Permit alterations are used to update a permit in cases where there is no increase in emission limits.

Future deployment of amine-based PCC capture plant of CO_2 will be associated with emissions of different pollutants in the gaseous and droplet phases to the atmosphere. These emissions can be reduced by deploying the appropriate control technology such water wash systems and demisters. If nitrosamines were found to be emitted at concentrations that may raise health concerns, UV destruction techniques (IEA GHG, 2012) or other techniques can used to resolve this issue.

Aspen-Plus PCC process simulations were used to provide a reasonable assessment for the emissions expected from the plant. The results obtained would depend on the accuracy of the inputs used to execute the simulations. The outputs of the Aspen Plus modeling scenarios provide the knowledge needed to determine which of these compounds should be targeted for further air quality modeling to determine its fate in the environment. The air quality assessment of emissions to air will need to address all expected plant operations including the business as usual operations. The air quality modeling results will be used to provide the required information for regulators, stakeholders, and the industry to assess the plant operation in terms of meeting the current air quality regulations. If emission levels are exceeding the implemented guidelines other control technology may be implemented to reduce selected compounds.

Emissions from PCC plants could contain chemical substances related to the used amines and their degradation products that may raise different environmental concerns. Consequently, industrial-scale PCC systems will be subject to pollution mitigation regulations. 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 (Azzi *et al.*, 2012). 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.

Ozone is not likely to be produced directly in the PCC process but it will be produced by secondary atmospheric chemical reactions (see *Fig. 1*). In addition to the criteria pollutants there is 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 (HAP) 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 Toxic Air Contaminants (TAC) such as the identified formaldehyde and acetaldehyde. Table 3 shows the potential contribution of each pollutants to atmospheric pollution where air quality regulations should be met.

TAC are defined as air pollutants that may cause or contribute to an increase in mortality or in serious illness, or may pose a hazard to human health. For these compounds there is no threshold level below which adverse health impacts may not be expected to occur even at low concentrations. Best available control technology for toxics is used to reduce these pollutants to the lowest possible level. A toxic-emission inventory would be required by regulators. This would also apply to the groups of nitrosamines and nitramines.

TABLE 3
Potential contribution of each pollutant to atmospheric pollution

Pollutants	Potential contribution to atmospheric pollution
MEA	Potential of photochemical smog oxidants formation
Ammonia	Secondary aerosols
DEA	Potential of photochemical smog oxidants formation
Formaldehyde	Potential of photochemical smog oxidants formation
Acetaldehyde	Potential of photochemical smog oxidants formation
Acetone	Potential of photochemical smog oxidants formation
Methylamine	Potential of photochemical smog oxidants formation
Amides	Secondary aerosols

The deployment of PCC units will affect the emission inventories for compounds that are anticipated to be emitted from the plant. It is expected that SO_x and NO_2 will be reduced during the PCC operations. However, volatile organic compounds and NH_3 will increase along with some other compounds such as amides and nitrosamines. There is also clear indication that aerosols would also increase as primary emissions from the plant and as secondary products produced by chemical reactions in the atmosphere. Appropriate air quality assessment of the potential impacts of the plant on human health and the environment would require the following:

- an updated emissions inventory that includes all major compounds that are expected to be emitted from the plant;
- atmospheric chemical reactions mechanisms describing the degradation of reactive species in the atmosphere.

Air emissions standards are also needed to evaluate exposure and health impacts resulting from different plant operating scenarios. All these requirements are to be understood before the deployment of commercial plants.

CONCLUSION

Amine-based post combustion capture of CO_2 technology is a readily available technology that can be used to reduce CO_2 emissions from coal fired power plants but it is important that emissions from the deployment of PCC meet the implemented air quality regulations.

The deployment of PCC will reduce SO_x and NO_2 emissions from the normal flue gas emissions. However, some other pollutants will be produced if appropriate control emission technologies were not adopted. Of these pollutants, NH_3 and aerosols emissions can be assessed with current air quality models to determine their air quality impacts. Attempts are being made to develop chemical reaction schemes to describe the photo-oxidation of MEA emissions and other amines. However, this topic is far from being complete and more research is still required to improve this area.

Current air quality guidelines may require to be updated to include limits for NH_3, nitrosamines and nitramines once more information related to their emissions is conclusive and being made available.

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REFERENCES

Angove D., Azzi M., Tibbett A., Campbell I. (2012) An Investigation into the Photochemistry of Monoethanolamine (MEA) in NO_x, *ACS Symposium Series* **1097**, 265-273.

Angove D., Jackson P., Lambropoulos N., Azzi M., Attalla M. (2011a) CO_2 Capture Mongstad-Theoritical evaluation of the potential to form and emit harmful compounds-Atmospheric Chemistry, http://www.gassnova.no/frontend/files/CONTENT/Rapporter/ProcessFormation_CSIRO.pdf.

Angove D., Jackson P., Lambropoulos N., Azzi M., Attalla M. (2011b) CO_2 Capture Mongstad-Theoritical evaluation of the potential to form and emit harmful compounds-Atmospheric Chemistry, http://www.gassnova.no/frontend/files/CONTENT/Rapporter/AtmosphericFormation_CSIRO.pdf.

Attalla M., Azzi M. (2009) Environmental impact of emissions from post combustion capture, IEA Greenhouse Gas R&D Programme, Regina Canada.

Attalla M., Azzi M. (2010) Environmental impact of emissions from post combustion capture, IEA Greenhouse Gas R&D Programme. Oslo, Norway, http://www.ieaghg.org/docs/General_Docs/Env_Impacts/4-Env%20Impact_CSIRO%20Attalla_Azzi.pdf.

Azzi M., Day S., French D., Fry R., Lavrencic S. (2012) Analysis of environmental legislative and regulatory requirements for the use of amine-based PCC in Australia. CSIRO Report prepared for the Australian National Low Emissions Coal R&D. www.anlecrd.com.au.

Azzi M. (2011) Environmental impacts of amine-based PCC plant, Presented at: *CLIMIT-Workshop: Amine emission from post combustion CO_2 Capture*, Oslo Norway.

Bedell S. (2009) Oxidative degradation mechanisms for amines in flue gas capture, *Energy Procedia* **1**, 771-778.

Brackstad O.G., da Silva E.F., Syversen T. (2010) TCM Amine Project: Support on input to environmental discharges. Evaluation of degradation components. Version 3, SINTEF F16202, Trondheim: SINTEF.

Chi S., Rochelle G. (2002) Oxidative degradation of MEA, *Ind. Eng. Chem. Res.* **41**, 17, 945-969.

Davis J. (2009) Thermal degradation of aqueous amines used for carbon dioxide capture, *Thesis*, University of Texas Austin.

Do T., Narendra D., Feron P., Azzi M. (2012) Process Modelling for Amine-based Post-Combustion Capture plant. Deliverable 3.2 Report prepared by CSIRO for the "Australian National Low Emissions Coal Research and Development".

European Commission (2013) Climate Action, http://ec.europa.eu/clima/policies/ets/index_en.htm.

Fluor (2004) Improvement in power generation with post combustion capture of CO_2. IEA GHG R&D Programme, Nov., Report No: PH4/33, 272.

GCCSI (2012) CO_2 capture technologies, Post Combustion Capture. http://cdn.globalccsinstitute.com/sites/default/files/publications/29721/co2-capture-technologies-pcc.pdf.

Goff G., Rochelle G. (2004) MEA degradation: O_2 mass transfer effects under CO_2 capture conditions, *Ind. Eng. Chem. Res.* **43**, 20, 6400-6408.

Goff G. (2005) Oxidative degradation of aqueous MEA in CO_2 capture processes, *PhD Dissertation*, University of Texas Austin, TX.

Gouedard C., Picq D., Launay F., Carrette P.-L. (2012) Amine degradation in CO_2 capture. I. A review, *Int. J. Greenhouse Gas Control* **10**, 244-270.

Grosjean D. (1991) Atmospheric chemistry of toxic contaminants: 6. Nitrosamines: Dialkylamine and N-nitrosomorpholine, *J. Air Waste Manage. Assoc.* **41**, 306-311.

Handbook of Gas Processors Suppliers Association (2004) 12th edition, Chap. 7, p. 5, GPSA.

IEAGHG R&D Program (2012) Gaseous Emissions from amine based PCC processes and their deep removal, Report 2012/07, http://www.ieaghg.org/index.php?/technical-reports-2012.html.

IPCC (Intergovernmental Panel on Climate Change) (2005) Special Report. Carbon Dioxide Capture and Storage, Summary for Policymakers. Intergovernmental Panel on Climate Change, http://www.ipcc.ch/pdf/special-reports/srccs/srccs_ summaryforpolicymakers.pdf.

Karl M., Dye C., Schmidbauer N., Wisthaler A., Mikoviny T., D'Anna B., Muller M., Borras E., Clemente E., Muñoz A., Porras R., Ródenas M., Vázquez M., Brauers T. (2012) Study of OH-initiated degradation of 2-aminoethanol, *Atmos. Chem. Phys.* **12**, 1881-1901.

Knudsen J., Andersen J., Jensen J. (2011) Results from test campaigns at the 1 t/h CO_2 PCC pilot plant in Esberg under the EU FP7 CESAR Project, *IEAGHG PCC1 Conference,* 17-19 May 2011, Abu Dhabi, UAE.

Koornneef J., Ramirez A., Turkenburg W., Faaij A. (2012) The environmental impact and risk assessment of CO_2 capture, transport and storage – An evaluation of the knowledge base, *Progr. Energ. Combust. Sci.* **38**, 62-86.

Lepaumier H., Da Silva E., Einbu A., Grimstvedt A., Knudsen J., Zahlen K., Svendsen H. (2011) Comparison of MEA degradation in pilot-scale with lab-scale experiments, *Energy Procedia* **4**, 1652-1659.

Masuda M., Mower H., Pignatelli B., Celan I., Friesen M. (2000) Formation of N-nitrosamines and N-nitramines by the reaction of secondar amines with peroxynitrite and other reactive nitrogen species, *Chem. Res. Toxicol.* **13**, 4, 301-308.

Moser P., Schmidt S., Stahl K. (2011) Performance of MEA in a long-term test at the PCC plant in Niederaussem, *Int. J. GHG Control* **5**, 620-627.

Pedersen S., Sjovoll M., Foastas B. (2010) Flue gas degradation of amines, *IEA GHG Workshop*, Oslo, 16 Fev.

Pitts J., Grosjean D., Vanmcauwenberghe K., Schmidt J., Fitz D. (1978) Photooxidation of aliphatic amines under simulated atmospheric conditions: Formation of nitrosamines, nitramines, amides, and photochemical oxidant, *Environ. Sci. Technol.* **12**, 946-953.

Reynolds A., Verheyen V., Adeloju S., Meuleman E., Feron P. (2012) Towards commercial scale postcombustion capture of CO_2 with MEA solvent-Key considerations for solvent management and environmental impacts, *Environ. Sci. Technol.* **46**, 3643-3654.

Sexton A., Rochelle G. (2006) Oxidation products of amines in CO_2 capture, Eight International Conference on Greenhouse Gas Control Technologies, GHGT-8, Trondheim, Norway, 19-2 June.

Sexton A., Rochelle G. (2009) Catalysts and inhibitors for oxidative degradation of MEA, *Int. J. Greenhouse Gas Control* **3**, 6, 704-711.

Sexton A., Rochelle G. (2011) Reaction products from the oxidative degradation of MEA, *Ind. Eng. Chem. Res.* **50**, 2, 667-673.

Strazisar B., Anderson R., White C. (2003) Degradation pathways for MEA in a CO_2 capture facility, *Energy Fuels* **17**, 1034-1039.

Sun Z., Liu Y., Zhong R. (2011) Carbon dioxide in the nitrosation of amine: catalyst or inhibitor? *J. Phy. Chem.* **115**, 26, 7753-7764.

Thitakamol B., Veawab A., Aroonwilas A. (2007) Environmental impacts of absorption-based CO_2 capture unit for post-combustion treatment of flue gas from coal-fired power plant, *Int. J. Greenhouse Gas Control* **1**, 318-342.

USEPA (2012) epa.gov/carbonpollutionstandard/pdfs/20120327 proposal.pdf.

Uyanga I.J., Idem R. (2007) Studies of SO_2 and O_2 induced degradation of aqueous MEA during CO_2 capture from power plant flue gas streams, *Ind. Eng. Chem. Res.* **46**, 2558-2566.

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