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OCTAVIUS

OPTIMISATION OF CO_2 CAPTURE TECHNOLOGY ALLOWING VERIFICATION AND IMPLEMENTATION AT UTILITY SCALE

Technical Memorandum

Object	Summary of the International Workshop on emissions from post-combustion CO_2 capture processes held on 13-14 February 2014 in Heilbronn (Germany)	
Dissemination level	**Public**	
Written By	Paul Broutin (IFPEN)	02/05/14
Checked by	Participants to the Workshop	12/05/14
Approved by the coordinator	Paul Broutin (IFPEN)	14/05/14
Main conclusions	*This Workshop has been a success in term of participation and information exchange.* *The main conclusion drawn is that there should not be any showstoppers in terms of emissions for most of the post-combustion CO_2 capture processes using amines as solvents.* *The knowledge developed and presented at this workshop shows that risks are much lower than previously reported for key configurations. It was found that potential environmental impact and risk assessment studies for preparation of discharge permits for industrial scale CO_2 capture units are highly case specific and should be evaluated separately for each case study.* *It is also important to continue research through international collaboration in order to develop standards in terms of emission levels and emission measurements.*	
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Content

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1 Introduction

This document compiles the summary of the international workshop on emissions from post-combustion CO_2 capture processes held on 13-14 February 2014 in Heilbronn (Germany). This conference which was hosted by EnBW has been organised by the EU FP7 OCTAVIUS project.

The programme of the workshop and the list of participants are given in an annex to this document. The programme and the presentations are available for download from the OCTAVIUS public website www.octavius-CO2.eu.

OCTAVIUS (**O**ptimisation of CO_2 **C**apture **T**echnology **A**llowing **V**erification and **I**mplementation at **U**tility **S**cale) is a FP7 European project dedicated to the demonstration of post-combustion CO_2 capture processes. Coordinated by IFPEN, the project brings together 16 other partners from the worlds of research and industry:

- 13 partners from 8 European Union and associated countries: TNO, SINTEF, Norwegian University of Science & Technology (NTNU), INERIS, Technical University of Denmark (DTU), Technical University of Hamburg-Harburg (TUHH), E.ON, EnBW, Doosan Power Systems, Enel Ingegneria e Ricerca, Laborelec (GDFSuez), EDF, Prosernat.
- 1 partner from the Russian Federation: Topchiev Institute of Petroleum Science (TIPS).
- 2 partners from South Africa: EcoMetrix and Eskom.

Main objectives of the workshop which gathered 33 scientists were to present the OCTAVIUS results on emission studies but also to share and discuss them with the invited organisations:

- Gassnova
- University of Oslo
- CO_2 Technology Centre Mongstad (TCM) & STATOIL (as observers only)
- The Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia
- University of Texas
- Electric Power Research Institute (EPRI)
- Consultancy for Environmental & Human Toxicology and Risk Assessment (CETHRA), France
- International Energy Agency Greenhouse Gas R&D Programme (IEAGHG).

A significant amount of progress has been made over the past few years since several other international meetings have been held on the state of the science, such as the IEAGHG/CLIMIT workshop in February 2010 and the EPRI workshop in May 2012. This information has led to a better understanding of emissions phenomena and the potential risks of post-combustion CO_2 capture processes with respect to these emissions.

These progresses were presented and discussed within the various sessions held which covered the following aspects:

- toxicology,
- sampling and analysis methods,
- emission measurements in pilot plants,
- degradation mechanisms,
- emission modeling and counter measures.

This conference was a success in terms of participation, quality of the discussions and information exchange.

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2 Workshop Summary

2.1 Session 1 : Introduction

After the hosts address delivered by **Dr. Arnim Wauschkuhn** (Director Energy Systems & New Technologies - EnBW), **Paul Broutin** (IFPEN) introduced the workshop by presenting the OCTAVIUS project, the programme and the objectives of the workshop.
These objectives were:

- To present and share the results of the OCTAVIUS project with the invited organisations
- To facilitate discussion around presented topics (by dedicated panel and discussions sessions)
- To draw conclusions regarding emissions measurements, control and mitigation with respect to post-combustion CO_2 capture.
- To disseminate the findings of the workshop to the wider audience of scientists, policy makers, industry and the general public.

Erik Gjernes (Gassnova) then reported the main results from the research activities on emissions sponsored by the Norwegian state**.** Through the important work carried out in Norway especially within TCM (CO_2 Technology Centre Mongstad) and for the preparation of the Full-scale CCS project in Mongstad, the knowledge on health and environmental effects of amines when used for CO_2 capture has been considerably improved. For TCM, the discharge permit has been obtained taking into account risk assessment based on amines health and environmental properties but also on dispersion studies. It was noted that currently NDMA toxicity was used to describe the toxicity of all nitrosamines and nitramines for the permitting of TCM. As further information on the toxicity of individual compounds becomes available, a less conservative approach may be possible in future. A follow-up study monitoring background levels of key compounds is currently in place.

Stephanie Shaw (EPRI) introduced the Working Group for Standardization of Amine Stack Sampling & Measurement Methods launched by EPRI in 2012 and presented where this working group was at the end of the previous workshop held in Palo Alto (CA) in May 2012. During this one, the importance of aerosol emissions in the form of mist was discussed, and the need for standardization of emissions sampling & analysis methods were highlighted. EPRI stated that the Working Group concluded that emissions below current detection limits could not be classed as unimportant with certainty and standards were required to improve this. International collaboration is necessary to efficiently develop these standards.

2.2 Session 2: Toxicology

Eladio Knipping (EPRI) presented the results from EPRI-Supported *in vivo* and *in vitro* amine toxicology experiments undertaken in cooperation with the Lovelace Respiratory Research Institute and NILU (Norwegian Institute for Air Research).

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It was reported that:
- Amines themselves are not a significant health hazard to the public at environmental concentrations: they are corrosive but not mutagenic.
- Nitrosamines are degradation products from amines reactions with nitrates/NO_x. Many are carcinogenic in animals. They are not stable in sunlight: lifetimes range from a few minutes to an hour. Many of these compounds can be captured efficiently by water-wash or with alternate methods.
- Nitramines may be formed at lower levels but are more light stable, longer-lasting than nitrosamines. They have a lower toxicity than nitrosamines. EPRI state that the overall concern is the current lack of available toxicology study data: there is a large array of potential nitramines of interest and animal cancer bioassay studies generally take 4-5 years and are extremely resource-intensive.

Amine toxicology studies on mice were carried out on monoethanolamine (MEA), methyl diethanolamine (MDEA), and piperazine (PZ) under oxidative, as well as oxidative and CO_2, degradation conditions. A smog chamber was used to investigate atmospheric transformation products.
The mice were exposed for 7 days to:
- neat amine,
- amine + degradation products,
- atmospherically aged/transformed materials (i.e., with secondary organic aerosol).

Two toxicological analyses were carried out:
- Lung inflammation, via bronchoalveolar lavage (*in vivo*),
- Genotoxicity/mutagenicity (*in vitro*).

An inflammatory response was observed only with exposure to O_2-degraded amines, pure amines and CO_2 degraded amines showed no response.
Two nitramines, methyl nitramine (MA-NO_2) and monoethanol nitramine (MEA-NO_2) of 5 tested showed mutagenic potential, but only at high doses.

Lisa Bertomeu (CETHRA) presented then the results in toxicology obtained within the Dalmatien project funded by ANR (The French Research Agency) which will end this year. Within this project, CETHRA is responsible for investigating the toxicological profiles and modes of action of the nitrosamines identified among the degradation products of MEA.

Different organs are targeted by 5 nitrosamines identified in the Dalmatien project: Liver (Li) is the most frequent, then oesophagus (Oe) and Nasal Cavity (NC):
- N-nitrosopiperazine (NPZ): oral route (rat) => NC and Li,
- N,N-dinitrosopiperazine (DNPZ): oral route (rat) => NC and Oe,
- N-nitrosomorpholine (NMOR): oral route (rat) => Li; mice => Li &Lung; Hamster=>Li, N-nitrosodiethanolamine (NDELA): oral route (rat and mice) => Li and NC,
- N-nitrosodimethylamine (NDMA): oral route (rat and mice) => Li and NC.

For each of these nitrosamines available data was presented in terms of:
- Pharmacokinetics
- Acute toxicity
- Sub-chronic and chronic toxicity
- Genotoxicity
- Carcinogenicity
- Reproductive and developmental toxicity.

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The metabolism of nitrosamines was also explained using NDMA metabolism as an example. Nitrosamines can either by detoxified by denitrosation to simple amines and aldehydes or activated to a diazonium ion that can form DNA adducts. Interestingly, it was noted that there appeared to be a poor correlation between the observed carcinogenicity and mutagenicity or nitrosamines.

A general exposure limit for nitrosamines (applied to the sum of carcinogenic N-Nitrosamines) has been established at 0.2 µg/m^3 (based on National Institute of Public Health; Québec - 2011).
In individual reports provided by CEHTRA on three nitrosamines (NPZ, DNPZ, NMOR), a more conservative limit of exposure for the general population is proposed: 0.58 to 7.9 ng/m^3.

In order to assess if a proposed capture project is under this level, it is necessary to model the atmospheric process sequence of emission, dispersion, transport, chemical conversion and finally deposition and realize measurements through exposure studies.
The main routes to reduction of impact are:
- Photolysis by sunlight (half –life for direct photolysis of NDMA vapour is about 5 to 30 min),
- Dispersion of the Nitrosamines into the atmosphere,
- Reaction of Nitrosamines with other molecules (e.g. O_2, NO_x).

2.3 Session 3 : Sampling and analysis methods

Stephanie Shaw (EPRI) presented the analysis methods developed within EPRI-supported studies and tested on laboratory-degraded amines. These degraded amine samples were also used for the toxicology studies described by Eladio Knipping (EPRI) in Session 2.
A multi-instrument approach has been found to be very useful in identifying degradation products. In these studies, High Resolution-Time Of Flight -Aerosol Mass Spectrometry (HR-ToF-AMS), combined with Electrospray Ionization Mass Spectrometry (ESI-MS), found both expected & new degradation products of common amines when used at low vaporization temperature. A double neutral loss method found additional nitrosamines beyond authentic standards.

Isaline Fraboulet (INERIS) presented the work carried out by INERIS within OCTAVIUS WP12.1, whose aim is to provide Standard Operating Procedures (SOPs) to be used for the characterization of pollutant emissions from CO_2 capture pilot plants.

Based on the review of existing methods (from literature, INERIS knowledge and information from OCTAVIUS partners),a roadmap was prepared including specific issues associated with CO_2 capture, recommendations and identification of gaps in knowledge on sampling & analysis methods methods. Recommendations on sample storage (cold environment protected from UV-light was recommended) have been also made. All this data has been used by INERIS to establish SOPs for a wide range of compounds including nitrosamines within WP12.1.

Within OCTAVIUS, nitrosamine measurement method evaluation is ongoing: two measurement campaigns will take place during the MEA campaign at the EnBW pilot plant in Heilbronn. A round robin test on synthetic liquid but also and samples containing nitrosamines will be undertaken by four OCTAVIUS partners; the results of which will also contribute to SOP validation.

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Solrun Johanne Vevelstad (SINTEF) presented the methodology for nitrosamine analysis developed by SINTEF.
LC-MS-MS-QQQ (liquid chromatography with triple quadrupole mass spectrometry) is used for analysis of specific degradation products.

Total nitrosamine analysis is performed by chemical conversion of the nitroso group (N-N=O) to NO gas which is then detected by chemiluminescence. This GC-MS-NCD concept developed by SINTEF allows high sensitivity (LoD < 50 ng/mL for NDMA).

Both methodologies are important tools for:
- Closing the gap between total nitrosamines and sum of single nitrosamines,
- Discovery of new nitrosamines,
- Understanding of amine chemistry.

Liang Zhu (University of Oslo) presented the results of on-line quantitative analysis on absorber emissions using PTR-TOF-MS at TCM. It is to be noticed that the length of the sampling line is important (100 m) but Liang confirmed that is not an issue for emission monitoring carried out in Mongstad.

2.4 Session 4 : Emission measurements on pilot plants

Purvil Khakharia (TNO) and **Jan Mertens** (Laborelec) presented results from aerosol testing on the mini-pilot plant at Karlsruhe University. The aim of these tests was to understand the impact of aerosols and soot particles on solvent emissions from a CO_2 capture absorber. Aerosol measurement was completed through two methods, UF-CPC (Universal Fluid Condensation Particle Counter) and ELPI$^+$ (Electrostatic Low Pressure Impactor). UF-CPC can only count the number of aerosol particles, whereas ELPI$^+$ allows counting but can also provide data on the size of the aerosol particles.

A clear impact of particles in flue gas on solvent emissions was demonstrated. Soot particles in the order of 10^6 per cm^3 leads to MEA emissions of 200 mg/Nm^3 and H_2SO_4 nuclei in the order of 10^8 per cm^3 leads to MEA emissions of 600-1100 mg/Nm^3. The impact of CO_2 concentration in the flue gas on the solvent emissions in the presence of particles was also presented; this work showed a maximum emission level at concentration of approximately 6 vol% CO_2. Therefore it was concluded that the plant operating parameter can have an impact on the overall extent of this phenomenon.

Measurement from ELPI+ has shown that H_2SO_4 aerosols are present in very high numbers (10^8/cm^3) and are very small (< 100 *nm*) and thus cannot be captured by traditional demisters. Additionally it was found that aerosols grow through the absorber, but most are still less than 1-2 µm and therefore not enough to be captured by traditional demister designs. The majority of the mass of MEA and water is in aerosols between the sizes of 0.5 and 2µm and therefore this is what new countermeasure should be aimed to eliminate this phenomenom.

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Paul Nielsen (University of Texas) presented the results of aerosol studies at bench and pilot scale plant undertaken by Steven Fulk at the University of Texas using the piperazine (PZ) solvent. He gave an overview of the campaign carried out in November 2013 at the SRP pilot plant which is based at the Pickle Research Center in Austin, Texas. Two tests were completed, first with H_2SO_4 Generator and the second with direct SO_2 injection.
It was observed:

- a reasonable agreement between manual sampling and FTIR,
- changes in aerosol size distribution from startup to steady-state,
- increase in Piperazine emission and plugging problems in presence of aerosol: if H_2SO_4 is turned on, a Piperazine emission pike is observed;
- the LVI produced a reliable particle size distribution, but the particle count was low compared to other studies at a max of $10^3/cm^{-3}$;
- increased emissions were observed with SO_2 injection;
- effect of temperature on SO_2 injection: if the intercooling is stopped, reduced emission are observed, but still above levels without SO2 injection.

It was noted that the campaign was short (only 2 days) but longer ones are planned.
From this campaign, it is concluded that SO_2 alone in the flue gases increases PZ emissions: so, a well designed and operated FGD/Polisher is critical.

Solrun Johanne Vevelstad (SINTF) presented then emission measurement from SDR rig operated by SINTEF. This Solvent Degradation Rig simulates typical process conditions for CO_2 absorption and desorption. It uses synthetic flue gas. Long term cycling of the solvent in a combined absorber and stripper setup gives combined degradation effects of absorber and stripper conditions. Duration each test was between 16 and 26 days, with the overall test period lasting 14 weeks. Degradation results are comparable to results seen on pilot plant (Einbu 2013).
All nitrosamines except NDMA were found to be below or close to detection limit. MEA-nitramine was also below the detection limit.
Process conditions were found to influence degradation and the emission profile:

- temperature, high oxygen and NO_x concentration increases degradation;
- temperature has also high influence on concentration of volatile products (ammonia and alkylamine).

Earl Goetheer (TNO) gave an overview of the work carried out on emissions within the OCTAVIUS project. He presented results obtained during emission measurements at the TNO pilot plant in Maasvlakte and from the ENEL pilot plant in Brindisi:

- It was proven at the TNO pilot plant that acid wash is excellent at reducing ammonia emissions, even with very high ammonia input concentrations (tested up to 150 mg/Nm^3).
- A Brownian demister has also been tested successfully demonstrated at the TNO pilot plant to eliminate the aerosol effect on solvent emissions. However, this technology imposes a very large pressure drop on the system and is therefore not practical for full scale applications.
- The Impact of Wet Electrostatic Precipitators on aerosol and emissions was explored at ENEL pilot plant in Brindisi. However the results were inconclusive as no aerosols were observed in Brindisi even when the WESP was turned off.

Two more emission campaigns are planned within the OCTAVIUS project on the EnBW pilot plant in Heilbronn.

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Scott Hume (DPS) presented process analytical techniques developed by Doosan Power Systems at the CCPilot100+ in Ferrybridge for online gas and liquid measurement:

- a Gasmet DX 4000 FTIR is used for online gas analysis. High reliability was achieved for gas sampling system and the FTIR. The FTIR was found to provide good detection of MEA and acid gases. It was also possible to profile CO_2 and O_2 concentration through the absorber. Maintenance of the FTIR unit is low.
- a Metrohm System was used for online liquid analysis. Deviation from laboratory analysis was low (~1% error on solvent concentration, ~5% error on solvent loading). So, results from online analysis are considered sufficiently accurate for control decisions but speed is not sufficient to deliver online process control (Metrohm analytical procedure takes respectively 7 and 13 minutes for solvent concentration and CO_2 loading). It has also to be noted that the system has high reagent consumption. A 'Hands on' approach is also necessary to maintain for reliability.

2.5 Session 5 : Emission measurements on pilot plants

Merched Azzi (CSIRO) presented an atmospheric chemical mechanism for MEA degradation. This model for MEA chemical transformation in the atmosphere has been developed and refined at CSIRO based on an amine oxidation mechanism which has been implemented into an air quality model (AQM) to take into account transportation, meteorology and deposition.
Experiments in smog chamber have been carried out to investigate amine photooxidation in presence of NO_x and other volatile organic compounds (VOC). Other amines than MEA have also been studied in smog chamber (Piperazine and AMP).
It has been confirmed in the smog chamber experiments that MEA is reactive in presence of nitrogen oxides and light, generating ammonia, amides and other compounds as reaction products, no nitrosamines have been observed during these experiments but low amounts of Nitramine were detected. It is noted that there was aerosol formation even though no seed particles were added to the chamber. For experiments with PZ both nitrosamines and nitramines were detected additionally significantly more aerosols were detected in PZ/NO_x compared to the MEA case.

MEA degradation model can predict key products concentrations for smog chamber experiments with MEA/NO_x but it requires further development to include the reactivity of other VOCs in the system. Semi-empirical adjustments have been made to mechanism to attempt to explain chemistry of compounds which are difficult to measure or identify. Additional reactions of MEA were included to simulate important removal processes that occur at night.
Chemical mechanisms for the other amines will be also investigated.
A new smog chamber is being built at CSIRO based on extensive knowledge acquired during amine degradation studies.

Paul Nielsen (University of Texas) presented on behalf of **Prachi Singh** (IEAGHG) on the techno-economic evaluation of reclaimer technologies for CO_2 post combustion capture: Prachi being ill, could not attend the workshop. This study was completed for two power plant cases, a pulverised coal and a natural gas combined cycle plant (NGCC). . Three solvents (MEA, PZ and MDEA/PZ). Three reclaiming technologies were considered: thermal reclaiming, ion exchange and electrodialysis.

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The main conclusions were presented:
- For the MEA case on coal flue gases, thermal reclaiming was found to be least expensive;
- For MDEA/PZ and PZ on coal flue gases, ion exchange and electrodialysis was found to be least expensive;
- For NGCC case, Ion exchange followed by electrodialysis was found to be least expensive;
- Solvent reclaiming was calculated to contribute 0.6-1.3% to the total electricity cost for coal and 0.3-0.4% for NGCC case;
- Polishing scrubber to reduce SO_2 in coal flue gas to <1 ppmv is highly recommended.
- Metal and mercury content in thermal reclaimer waste from coal-fired power plant would cause classification as hazardous in US, increasing disposal cost;
- In the EU the thermal reclaimer wastes from both the coal-fired and NGCC power plants would likely to be considered hazardous;
- The waste streams from the ion exchange and electrodialysis waste contain up to 95% water. In the US regulations these wastes will not be classified as hazardous, whereas in the EU due to PZ classified as sensitizing, the reclaimer waste from ion exchange and electrodialysis process for PZ and MDEA/PZ solvent may be classified as hazardous;
- Thermal reclaimer waste can be disposed in a cement kiln or by co-firing into the boiler at power plant. This will require additional regulation to be considered as well as the impacts on emissions of these processes;
- Ion exchange and electrodialysis reclaimer waste is diluted waste and could potentially be disposed of in waste water treatment plant. However this will require additional equipment to a standard power plant waste water treatment plant.

IEAGHG would like to recommend that the characterization of reclaimer waste from a real plant is very important in order to determine the procedure for waste handling and identify the most suitable waste disposal options.

Pierre-Louis Carrette (IFPEN) gave then an overview of the DALMATIEN (Degradation of Amines in Liquid Matrix and Analysis: Toxicity or Innocuousness for ENvironment?) project coordinated by IFPEN. The objectives of DALMATIEN are:
- to identify amine degradation products (by developing analysis methods),
- to understand their formation,
- to assess their toxicity.

A new sampling method (HS-SPME) has been developed for volatile products with a reduced matrix effect which allows detection of minor products.
Several new Pyrazine and alkylpyrazines compounds have been identified in MEA in the liquid phase using HS-SPME. These products were detected at IFPEN & EDF pilot plants. A mechanism for their formation has been proposed based on the literature.

A toxicity assessment has been also undertaken by CETHRA on these compounds:
- these compounds were found to be eye & skin irritants,
- they were found to have no genotoxic potential,
- pyrazine derivatives are considered as safe by FEMA (Flavor and Extract Manufacturers Association).

Same study will be undertaken with piperazine.

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Alexey Volkov (TIPS RAS) presented the first results on MEA reclaiming within the OCTAVIUS project. Within this project, TIPS RAS is responsible for the design, manufacture and preliminary tests of an electrodialysis test module for solvent reclaiming. This process is designed for the removal of heat stable salts (HSS) from the MEA solvent and has been tested at the EnBW pilot plan in Heilbronn.

Alexey described in detail the EDM (Electro Dialysis Module) which has been successfully designed, built, commissioned and operated.

Stable EDM performances have been observed during pilot testing with real degraded solvent and successful removal of HSS content from real solvent as shown by the presented results after 400 hours of continuous pilot plant operation. An increase of the EDM process efficiency was observed with higher HSS concentrations in the solvent to be treated.
Analysis of solvent after 535 hours is ongoing.

2.6 Session 6 : Emission modelling and possible counter measures

Merched Azzi (CSIRO) presented a case study completed by CSIRO on air quality assessment for emissions from a post-combustion CO_2 capture plant using MEA as solvent. Loy Yang power plant located in Victoria (Australia) was the basis of this investigation. For this study, the amine chemical mechanism developed using smog chamber experiment data coupled to air quality models was used.

Main conclusions of this study were the following:
- The atmospheric concentration limits for ammonia and MEA are 830 ppb and 100 ppb respectively (EPAV 3min avg.). The latter is much higher than the MEA concentrations predicted by the model which peaked at 2.0 10^{-4} ppb. There is a peak of ammonia emissions for a short period of time (1 hour at start-up) but concentrations near the plant are comparable to concentrations resulting from soil fertilisation north of the power station.
- It can be seen that the average nitrosamine concentrations lie in the range 10^{-14}–10^{-13} ppb, and the average nitramine concentrations lie in the range 10^{-12}–10^{-11} ppb. In the case of nitrosamine this lies well below the suggested air quality guideline of 0.6 x10^{-4} ppb at 298K, assuming a molecular weight of 118 g/mol.
- The secondary reactants such as nitrosamine and nitramine show less than linear increases, possibly as a result of the production rates being limited by other factors such as hydroxyl radical availability and environmental conditions.

Eladio Knipping (EPRI) presented on the atmospheric chemistry of amines.
Amines form secondary aerosol through a complex mixture of salt formation (including aminium nitrate and sulfate) which are oxidized. Aminium salt formation is perhaps the dominant atmospheric aerosol formation mechanism, though the thermodynamics remains uncertain (better characterization needed).

Amines direct oxidation reactions occurs also with NO_x and ozone (photooxidation).
It was observed that oxidation of tertiary amines forms significant aerosol whereas oxidation of secondary or primary amines does not form significant aerosol.

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Paul Nielsen (University of Texas) gave an overview of the work carried out by Nathan Fine at University of Texas on nitrosamine formation in amine scrubbing. At first, he explained the nitrosamine cycle:

- NO_2 removal by polishing scrubber,
- NO_2 absorption (reaction with solvent in the absorber),
- Nitrosation from nitrite (in the stripper).

To estimate formation rates of nitrosamine several experiments were undertaken. These experiments included wetted wall column experiments to high gas flow absorption and thermal cylinder experiments.

Main conclusions of the experimental studies and pilot plant results are the following:

- Rate of NO_2 absorption decreases tertiary> secondary > primary amines. NO_2 absorption in amines produces mostly nitrite.
- Nitrosation in primary and secondary amines is carbamate catalysed. Nitrosamine yield depends on loading, carbamate stability, and pK_a, concentration of secondary amine byproducts in primary solvents. Tertiary amines do not nitrosate rapidly. Blends with PZ and tertiary amines will nitrosate to MNPZ.
- Accumulation will be limited by decomposition in stripper.

Purvil Khakharia (TNO) presented then the work carried out by NTNU and TNO within the OCTAVIUS Project on degradation and emissions modelling and comparison with pilot plant results for MEA.

The types and overall extent of degradation products from MEA are reasonably predicted by the proposed model: good fit with lab experiments. However, in lab experiments auto-catalytic process are not observed but are present in pilot plant testing's. Additionally the composition split between degradation products is significantly different between lab scale tests and pilot plant operation. Further explanation/hypothesis are necessary for pilot plant results in relation to the causes of auto-catalytic chemistry that is experienced.

For emissions modelling, TNO has developed an approach for aerosol calculation using Aspen Plus. The importance of the supersaturation/temperature bulge was confirmed by modeling results. The semi-rigorous model are in agreement with trends from experimental results from the mini-pilot plant at Karlsruhe Institute of Technology.

Odd Gunnar Brakstad (SINTEF) presented the work from SINTEF on biodegradation of nitrosamines and nitramines in the aquatic environment. Aquatic fate and degradation processes are complex: hydrolysis, photodegradation, adsorbance to sediment particles, bioaccumulation, and biodegradation all have to be considered. Sixteen nitrosamines and nitramines were tested in different biodegradation experiments. None of the compounds were ready biodegradable by screening testing.

Studies with normal water as bacterial source showed that:

- compounds with hydroxyl groups are biodegradable;
- biodegradation is temperature dependent;
- results from experiments with different water sources mainly show comparable results.

Predictions of possible biodegradation products have indicated that:

- Slowly biodegradable alkyl-nitrosamines and nitramines may be generated from alkanol-compounds,
- Nitrosamines may be transformed to nitramines.

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Hanna Knuutila (NTNU) presented experiences carried out at NTNU on destruction of NDELA in 30 wt% MEA and 50 wt% DEA solutions in a pilot using UV-light.

The following has been studied:
- the formation of NDELA in 30wt% MEA and 50wt% DEA with NO and NO+NO_2 present in the gas phase,
- the destruction of NDELA in these solutions with UV-light.

Pilot experiments have shown that the decomposition of NDELA decreases with increasing the colour of the solution and the amine concentration.
In the main solvent loop the decay rate of NDELA is low for both MEA and DEA. It is explained by a huge decrease of the penetration depth when the solvent is coloured by degradation products. So, the use of UV-light in the main solvent loop would require an optimization of the UV-light reactor.

The UV-light reactor was also tested in water wash circulation. In this application it was found that NDELA decomposes very fast, it was noted that the water wash remains clear: therefore there is no impact of colouration.

2.7 Session 7 : Discussion

The modelling case study realized by CSIRO on air quality assessment for emissions from a full scale Post-Combustion CO_2 Capture plant using MEA as solvent confirmed that the expected amount of MEA and Nitrosamines at the ground level would be extremely low. For this study concerning the Loy Yang power plant located in Victoria (Australia), the amine chemical mechanism developed using smog chamber experiment data was used coupled to air quality models.

It is of course necessary to wait for the feedback in term of emissions monitoring from the first full scale demo plants such as the Boundary Dam project with capture and storage of 1 $MtCO_2$/year from coal combustion flue gases that will start in 2014. Nevertheless, we may conclude that up to now there should not be any showstoppers in terms of emissions for most of the post-combustion CO_2 capture processes using amines as solvents.

Toxicology assessments are difficult but can be done as relative to other compounds. In Norway, the risk assessment for TCM is based on total sum of nitrosamines and nitramines considered as NDMA.

Amines themselves are not mutagenic at environmental concentrations, but degradation products can be. Toxicity tests on mice showed that solvent, that is degraded in the laboratory with CO_2 and then exposed to atmospheric conditions and aged, caused no significant increase in toxicity compared to the control.

In lab degradation and in vivo exposure studies - degradation of amine in O_2 was more extensive than when CO_2 present. Mutagenic and cytotoxic effects were observed only at highest doses of atmospherically-aged degraded amine mix.

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What is the appropriate risk level?: it appears very important to define standards for emissions level through international collaborations .

Through international collaborations such as the EPRI working group, it will be also possible to develop standards for emission measurements. For instance, round robin tests are essential in order to validate Standard Operating Procedures (SOPs) for sampling and analysis methods. This process is made more efficient and effective if many methods and laboratories can be involved. If no chemicals of interest are seen, is that because LoD are too high? Because it is not a good method? Because the products are not present? How conservative do we have to be? But on other hand not detectable does not mean not important.

The OCTAVIUS project is trying this approach by organizing in April 2014 a round robin test on gas and liquid samples from the campaign on the EnBW pilot plant including also synthetic prepared samples. The 4 concerned partners (SINTEF, E.ON, INERIS & IFPEN) invite other labs to join on their own costs (e.g. UT Austin, EPRI, CSIRO, TCM, Gassnova...).

Aerosol formation is also an important issue as it impacts emissions. They are caused by many acid gas nuclei which condense. SO_3 and particulates, and other flue gas parameters, are drivers of this mist formation but aerosols formation has not been observed on all the industrial pilot plant and it is crucial to understand why. For that, it is necessary to consider the power plant to capture plant gas path to explain the origin of the aerosol effect (e.g. coal type, SCR, GGH, FGD and pre-scrubber).
Different measurement technologies are available for particle counting and size distributions, but there are very high sensitivity to sampling conditions.

Several counter-measures for avoiding the formation and the effect of aerosols are being investigated and patented: these technologies have been successfully tested within the OCTAVIUS project and at University of Texas.

There is also a great need for identification and validation of measurement techniques that work and are practical to apply regularly without advanced trained personnel, with detailed public documentation on methods. Emission monitoring will be necessary for the future industrial units of post-combustion CO_2 capture.

Last but not least, experiments to determine the fate of emissions in the atmosphere with photo-catalytic effects and reactions with atmospheric species is key to develop models to complete environmental impact assessment. Smog chamber testing is necessary to improve mechanisms to run the air quality models.

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3 Main Conclusions and Recommendations

The main conclusion drawn from the workshop is that there should not be any showstoppers in terms of emissions for most of the post-combustion CO_2 capture processes using amines as solvents.

The knowledge developed and presented at this workshop shows that risks are much lower than previously reported for key configurations.

It was found that potential environmental impact and risk assessment studies for preparation of discharge permits for industrial scale CO_2 capture units are highly case specific and should be evaluated separately for each case study.

The aspect of aerosol based emissions has drawn considerable interest recently. Much progress has been achieved in understanding this phenomenon from both theoretical and experimental point of view. Further work must be undertaken to study mist composition, various countermeasures and its techno-economic feasibility to address this issue.

It is also important to continue research through international collaboration in order to develop standards in terms of emission levels and emission measurements.

A round robin test on synthetic liquid and gas samples containing nitrosamines will be organized by the OCTAVIUS project and other labs are invited to join.

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4 ANNEX

- Final Programme of the Workshop
- List of Participants

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Programme of the OCTAVIUS Workshop on Emissions from CO_2 Postcombustion capture processes

Day 1: Thursday 13 February

08:30 – 08:45 **Welcome**
Hosts Address by **Dr. Arnim Wauschkuhn (Director Energy Systems & New Technologies - EnBW)**

08:45 – 10:00 Session 1: Introduction (Chaired by Paul Broutin)

Paul Broutin (as OCTAVIUS coordinator): Objectives of the workshop
Erik Gjernes (Gassnova): Main results from the research activities on emissions sponsored by the Norwegian state
Stephanie Shaw (EPRI): Lessons from the previous workshop held in 2012 at Palo Alto (Ca)

10:00 – 11:00 Session 2: Toxicology (Chaired by Pierre-Louis Carrette)

Eladio Knipping (EPRI): Toxicology experiments, including in vivo as well as in vitro testing of degraded amines
Lisa Bertomeu (CEHTRA): The toxicological profiles and Modes of Action of the Nitrosamines identified among the degradation products of MEA and the Determination of the Acceptable Exposure Levels for the general population via inhalation route.

11:15 – 12:30 Session 3: Sampling and Analyses methods (Chaired by Scott Hume)

Stephanie Shaw (EPRI): Methods for estimating amine emissions
Isaline Fraboulet (INERIS): Recommendations regarding methods to be used for the characterisation of emissions from CO_2 Postcombustion capture processes
Solrun J. Vevelstad (SINTEF), Liang Zhu (U. Oslo): Method for Nitrosamines analysis.

14:00 – 16:00 Session 4: Emission measurements on pilot plants (Chaired by Sven Unterberger)

Purvil Khakharia (TNO) Jan Mertens (Laborelec): Results from Aerosol testing at Karlsruhe University
Paul Nielsen (UT): Aerosol Formation and Bench Scale and Pilot Measurements (Work by Steven Fulk)
Solrun Johanne Vevelstad (SINTEF): Emission measurements from SDR rig.
Earl Goetheer (TNO): Results from OCTAVIUS campaigns on TNO & ENEL pilot plants
Scott Hume (Doosan Power Systems): CCPilot100+ Experience with Process Analytical Methods

16:30 – 18:30 Session 5: Degradation mechanisms (Chaired by Chris Satterley)

Merched Azzi (CSIRO): Development of an atmospheric chemical mechanism for MEA degradation
Paul Nielsen: Evaluation of reclaimer disposal for CO_2 Postcombustion capture **(Work by Prachi Singh IEAGH)**
Paul Nielsen (UT): Oxidative Degradation of Amines, Bench and Pilot scale studies, rates in cyclic systems, degradation products from pilot plants
Pierre-Louis Carrette (IFPEN): Results from the DALMATIEN project
Alexey Volkov (TIPS RAS + EnBW): MEA Reclaiming - results from EnBW campaign carried out within the OCTAVIUS project

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Day 2: Friday 14 February

08:30 – 10:30 Session 6: Emissions modelling and possible counter (Chaired by Earl Goetheer)

Merched Azzi (CSIRO): Air quality assessment for emissions from a PCC plant – a case study
Eladio Knipping (EPRI): Atmospheric Chemistry of Amines
Paul Nielsen (UT): Formation and Fate of Nitrosamines in the Process – Bench scale studies on NO_2 absorption, nitrosamine formation rate and stoichiometry, nitrosamine thermal degradation and products for Piperazine, MEA, MDEA, other amines and blends (work by Nathan Fine)
Purvil Khakharia (TNO + NTNU): Results from the OCTAVIUS Project.
Odd Gunnar Brakstad (SINTEF): Degradation of nitrosamines og nitramines in the environment, with focus on biological degradation
Hanna Knuutila (NTNU): Experiences on destruction of NDELA in 30 wt% MEA and 50 wt% DEA solutions in a pilot using UV-light

11:00 – 12:30 Session 7: Discussion

Research Priorities and Guidelines for full scale demonstration

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Participants to the OCTAVIUS workshop on emissions

First Name	Last Name	Organisation
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Camille	GOUEDARD	IFPEN
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Sören	EHLERS	TUHH
Chris	SATTERLEY	E.ON
Laurence	ROBINSON	E.ON
Bernd	SCHALLERT	E.ON
Peter	RADGEN	E.ON
Armin	WAUSCHKUHN	EnBW
Sven	UNTERBERGER	EnBW
Alexander	RIEDER	EnBW
Jens	BAUER	EnBW
Scott	HUME	DOOSAN
Jovita	JUODAITYTE	ESKOM
Jan	MERTENS	Laborelec/ GDF SUEZ
Domitille	BONTEMPS	EDF
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Erik	Gjernes	GASSNOVA
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