PROPOSAL FOR A TEST PROTOCOL FOR EVALUATION OF SOLVENTS

-

PROCESS AND ATMOSPHERIC CHEMISTRY

Tel-Tek
Kjølnes ring 30, Porsgrunn
Norway

H&E TQP Amine
CCM project frame agreement
256430116

Report 2210040-1
October 2010

Preface

This Test Protocol has been developed by Tel-Tek under contract with the Carbon Capture Mongstad (CCM) project (Gassnova frame agreement 257430116, contracts 257430117 and 8).

Project co-workers:

Professor Dr. Klaus J. Jens, Telemark University College and Tel-Tek, Porsgrunn, Norway, responsible for in-process chemical reactions.

Dr. Siw B. Fredriksen, Norner Innovation, Stathelle, Norway, responsible for in-process chemical reactions.

Professor Dr. Dag Eimer, Tel-Tek, Porsgrunn, Norway, responsible for chemical engineering.

Professor Dr. Claus J. Nielsen, Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry at the University of Oslo, Norway, responsible for the study on the gas-phase atmospheric reactions.

Professor Dr. Hartmut Herrmann and Dr. Dirk Hoffmann, Leibniz-Institut für Troposphärenforschung, Germany, responsible for the study on the aqueous phase atmospheric reactions.

Siv.ing. Jon Hovland, Tel-Tek, Porsgrunn, Norway, project manager and quality assurance.

REFERENCE PAGE

Document 2210040-1	*Ref. Nr.* 2210040-1	*Date:* 25.10.2010

Author (s) in alphabetical order Dag Eimer Siw Fredriksen Hartmut Herrmann Dirk Hoffmann Jon Hovland Klaus Jens Claus Nielsen	*Tel-Tek Security Classification* Internal *Pages/ Appendices* 20/-
Title Test Protocol for the evaluation of amine solvents for Carbon Capture.	*Project Title* H&E TQP Amine4 *Project nr.* 2210040
Customer CCM project / Gassnova	*Customers ref.* 257430116

Resumé

The amine solvent technology for carbon (CO_2) capture from flue gases may lead to emissions of amines and compounds formed from amines. These emissions may be harmful or through chemical reactions in the atmosphere be converted to harmful compounds. This report proposes a Test Protocol, a set of actions to investigate the formation of compounds in the CO_2 capture process, emission of compounds from the process, and the formation and fate of compounds in the atmosphere after emission.

Project leader Jon Hovland	*Approved (Projects > 10.000 NOK)*
Department Leader Hans Aksel Haugen	*Approved (Projects > 100.000 NOK)*

Descriptive Words

English	*Norwegian*
Carbon capture	Karbonfangst
Amine	Amin
Emission	Utslipp
Atmosphere	Atmosfære

Fil ref.: @RappskE.dot

Table of contents

1. INTRODUCTION

Carbon dioxide capture with amines is an established technology, e.g. for gas sweetening. In order to reduce CO_2 emissions, it has been proposed to introduce large scale carbon capture (CC) and storage.

One technology used for post-combustion carbon capture is absorption in amine solvents. So far the technology has mainly been used for producing CO_2 for industrial use. In case this technology is taken into use for large scale CCS, a more in depth evaluation of the consequences are needed. Amines and degradation products of amines and additives may be emitted with the flue gas from the CC plant. Further, by reactions in the atmosphere harmful substances may be formed (Pitts et al., 1978).

1.1 The CCM (Carbon Capture Mongstad) project

Statoil will build a gas-fired power plant in conjunction with the refinery at Mongstad in western Norway (county of Hordaland). According to the agreement between the Norwegian government and Statoil CO_2 from the power plant shall be captured. More information is available on Statoil's home page.
http://www.statoil.com/en/TechnologyInnovation/NewEnergy/Co2Management/Pages/Mongstad.aspx

The CCM project is developing concepts for an amine based post-combustion CO_2 capture plant at Mongstad. One activity in the project is to evaluate the health and safety issues related to the possible amine emissions from the plant. This Test Protocol is a proposal for a study to determine which chemicals may be emitted from a CC plant, as well as the chemical reactions that may take place when amines enter the atmosphere. The ouput from the Test Protocol will be used for dispersion modelling and for health and safety evaluations, e.g evaluation of exposure and toxic effects.

2. AMINES

Typical amines used for CO_2 absorption are monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), methyldiethanolamine (MDEA), and piperazine (PZ).

Literature reviews carried out on behalf of the CCM projects for these amines have shown that there is insufficient knowledge about the formation and emission of harmful compounds from CC plants. Systematic testing is required to reduce risks.

For the purpose of this protocol it is assumed that full amine solvent formulation is known. It is assumed that industrial grade chemicals are used in the preparation of the solvent. Such chemicals usually contains impurities, which must also be known.

3. TEST PROTOCOL

3.1 Objective

The objective of the Test Protocol is to describe a procedure to uncover the properties of an amine solvent with respect to forming and emitting potentially harmful chemical compounds. It covers the formation of harmful compounds in process as well as by atmospheric reactions post emission.

The Test Protocol is one step in the qualification programme and has relation to other CCM project activities as indicated below

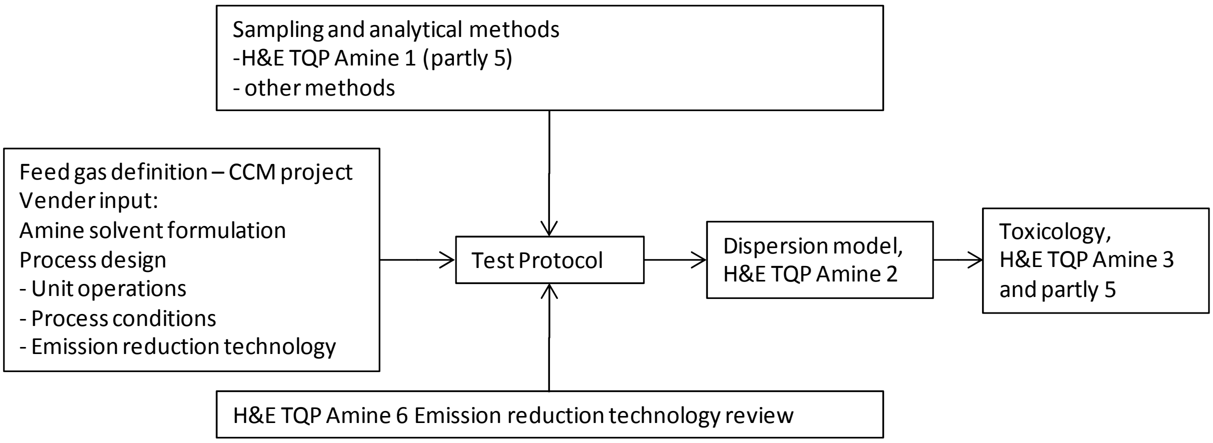

Figure 3.1-1 Scheme showing input to the Test Protocol and the position relative to other H&E TQP Amine activities.

3.2 Health and safety

Health and safety must be considered in all phases of the execution of this Test Protocol. Risks shall be minimised through relevant mitigating actions and using best practice. HSE activities shall be according to national law, best practice, and the requirements of the CCM project. The solvent vender must disclose all relevant information to protect personell and ensure safe handling of the solvent.

The organization carrying out the Test Protocol shall implement a Risk Management System in accordance with the principles and guidelines provided in ISO 31 000 Risk Management Guidance Standard or equal. For the purpose of this Test Protocol this includes (but is not limited to):

- Safe job analysis
- Use of personal protective equipment (*e.g.* glasses, gloves, clothing)
- Using as small amounts of hazardous chemicals as practically possible
- Safety data sheets (SDS) for all chemicals
- Work in closed systems and/or systems with adequate ventilation (*e.g.* use of fume hoods)
- Safe use of equipment (*e.g.* pressure vessels) and chemicals
- Safe handling of waste and disposal of chemicals

3.3 Quality

The organization shall have implemented a Quality Management System in conformance with the specified requirements in NS-EN-ISO 9001 (latest edition) or equal. The System shall be documented, approved and signed by the organization's top management.

For the purpose of this Protocol special attention should be paid to assuring that the requirements of section "7.6 Control of monitoring and measuring devices" in the 9001 standard are adhered to.

All work carried out shall be in accordance with accepted standards for scientific work intended to be published in recognised international peer-reviewed journals within the relevant fields.

3.4 Documentation and records

The work shall be documented and recorded to give full traceability from: experimental design, use of equipment and methods, output from monitoring and measuring; to the results, conclusions and recommendations presented. Documentation and records shall be in accordance with section "4.2.4 Control of records" in the ISO 9001 standard.

Electronic records shall be in an open format, e.g. PDF, TIFF, or a format approved by the CCM project. Some computer controlled monitoring and measuring equipment use proprietary file formats and special attention must be given to output from these.

Records shall be kept for a time period to be agreed with the CCM project.

Specifically the following items shall be documented according to best practice in international peer-reviewed journals within the respective scientific fields (chemical engineering, physical, organic, inorganic, analytical, and atmospheric chemistry).

- Documentation of amine solvent composition
- Documentation of feed gas composition
- Equipment and reaction vessels/chambers for amine degradation
- Instrumentation and analytical methodologies
- Documentation of transfer lines/systems between reaction vessel/chamber on on-line and off-line and sampling devices.

Note: In the different scientific fields the terminology (mainly due to historic reasons) is often specific to the field. In this Test Protocol scientists from different fields will have to cooperate. To avoid misunderstandings it may be necessary to clearly define terms used and also explain similarities and differences in the terms used.

3.5 General scheme

The general scheme to be followed for the Test Protocol is outlined in the figure below:

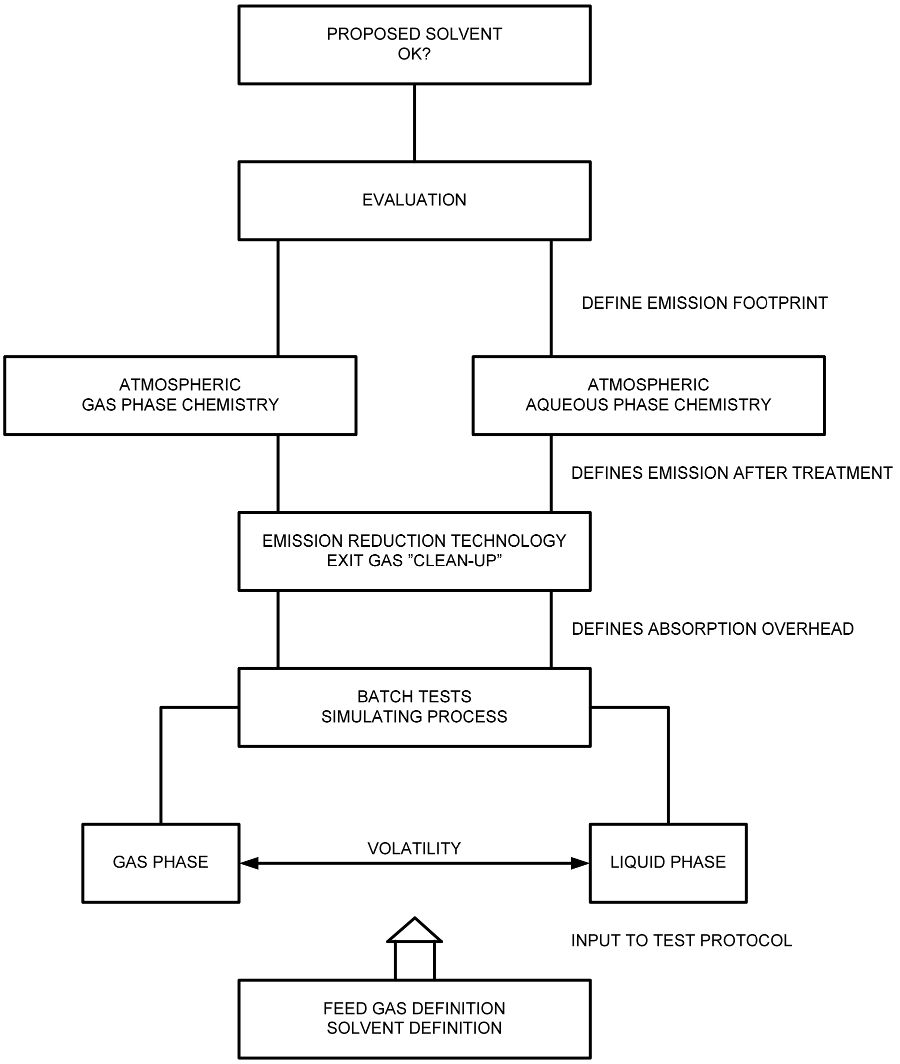

Figure 3.5-1 General scheme for Test Protocol

Note: Given the present overall time frame for the CCM project we do not foresee that it is possible to determine in detail all chemical reactions and parameters for all compounds detected. There must be a selection of which compounds, chemical reactions and mass transfer parameters that shall have priority. The selection will partly depend on factors outside the scope of the Test Protocol such as exposure routes and toxic effects. We suggest that the CCM project shall organize the activities accordingly to achieve this objective.

3.6 Literature review

A literature review shall be prepared as a part of the test protocol. The study shall as far as possible be based on scientific literature from peer reviewed journals and books. However, in cases where peer reviewes literature are not available, also other open literature (conference proceedings, presentations, reports) can be referred to. It may be prudent to include such literature, e.g. if hazards are discussed, but appropriate reservations should be made. If internal or confidential literature is used, this shall be made available to the CCM project.

The scope of the study is to review and summarize the degradation products that have been reported from the amine and other compounds in the solvent. Special focus shall be the possible formation of harmful compounds.

The CCM project has commissioned a number of studies as part of the health and environment total quality progamme (H&E TQP) with relevance for this protocol:

- Establish sampling and analytical procedures for potentially harmful components for post combustion amine based CO_2 capture
- Modelling of atmospheric dispersion of components from post combustion amine based CO_2 capture
- Protocol for evaluation of solvents - emission mixture tqxicity
- Nitramines analysis procedures development and screening toxicity study
- Emission reduction technologies

At time of writing the reports from these studies are not available. They should be reviewed as part of the development of this Protocol in order to integrate the findings and recommendations into this Protocol.

3.7 Emission reduction technology review

Flue gas may contain aerosols and/or droplets as well as volatile chemicals. In addition the entrained liquid phase may contain non-volatile substances. Technology to reduce aerosols and droplet emission will selectively reduce the emission of non-volatiles. Emission reduction technologies (ERT) may also be specific in relation to properties of the chemicals emitted (e.g. basic compounds will be absorbed in an acid wash). Any chemicals used for ERT may also represent a harmful emission, directly or through its potential reaction products.

No specific ERT other than a “base case” water wash and a nonspecified demister has been assumed for this Test Protocol, according to input given in Invitation to tender..

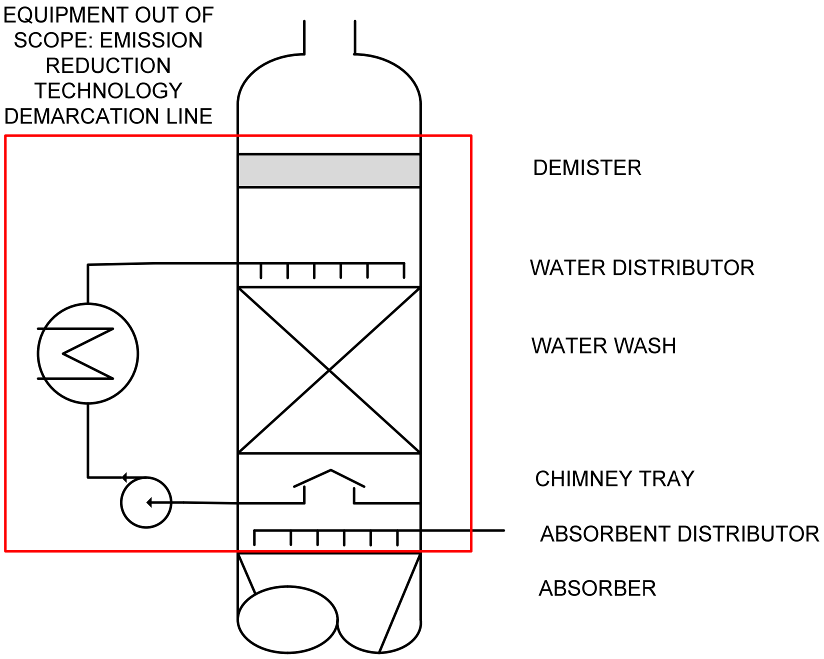

Figure 3.7-1 The conventional or “base case” ERT section in the top of the CO_2 absorption column. The red box defines equipment not considered in detail in this report.

The ERT is the scope of a separate project of the CCM project qualification. Once a specific case is considered an evaluation of the ERT should be performed in the case that modifications to the Test Protocol are needed. The function of the water wash and the demister is to recover chemicals that would otherwise be emitted. The recovery fraction will probably vary from chemical to chemical in the gas phase. The Test Protocol must allow the technology provider to specify recovery factors for chemicals on a one by one basis. The vender must supply an estimate of aerosol emission, kg/hr, and droplet size distribution. This means that what is estimated to be emitted from the CO_2 absorption section (absorber in the figure), may not necessarily be the same as emitted to the atmosphere. If a technology provider makes such claims, the Test Protocol shall demand that these claims are substantiated. Such validation may include models, measurements from pilot or full scale plants.

3.8 Analytical methods

The H&E TQP amine project has in a separate project established sampling and analytical procedures for potentially harmful components from post combustion amine based CO_2 capture; including:

- Design of sampling point in treated flue gas
- Manual sampling procedures
- Online analysis
- Literature survey of existing analytical procedures and recommendations
- Establishing analytical procedures

These sampling and analytical procedures developed for the CCM project shall be part of this Test Protocol when appropriate or requested. A review, including risk evaluation, shall be carried out to ensure that these analytical procedures are appropriate for the amine solvent to be tested. If necessary alternative analytical methods shall be proposed and approved by the CCM project.

3.9 In process formation and emission of substances

3.9.1 Output

The output of this part of the Test Protocol shal be, as minimum, the identification of in-process produced volatile compounds and their rate of desorption at the top of the absorber column. The rate shall be given as kg/hr at a stated gas flow. The emission to the atmosphere shall then be calculated based on ERT recovery factors (cfr section 3.7) and aerosol emission data supplied by vender or any other party appointed by the CCM project.

3.9.2 Description of the work sections

The strategy for meeting the output requirement is divided into four work sections:

1) Identification of compounds produced in a) absorber conditions and b) stripper conditions. This step is to be run in dedicated batch autoclaves and requires closed mass balances. It is considered necessary to perform experiments in separate vessels to clearly identify the reactions taking place and products formed under absorber and stripper conditions respectively. However, it is to be shown that no synergistic effects due to the separation of the thermal and oxidative step are missed.
2) Transfer of an aged solution into a Vapour Liquid Equilibrium (VLE) cell. Determination of partition coefficients of the volatile compounds.
3) Determination of the steady state rate of formation of the compounds identified in 1). This work section will utilize standard chemical engineering knowledge to model the rate of continous, steady state in-process formation of the volatile products identified in

work section 1) based on the batch reactor data.
4) Combination of the result of work section 3 with work section 2 will give the target output; i.e rate of desorption of volatile components at the top of the absorber column.

A batch autoclave is chosen for the degradation experiments since this is a common equipment type and satisfactory amine reaction control and analysis are expected to be possible. Furthermore, it is well known chemical engineering practise to model reaction conversion and selectivity of a continous flow reactor based on batch reactor data.

3.9.3 Minimum requirements of experimental analysis

1) All volatile degradation products shall be identified and quantified.
2) All models shall be documented.
3) Mass balance closure (N, C) > 80 %.

3.9.4 Specific chemical tests (Target analysis).

1) Test for primary, secondary and tertiary amines in the liquid phase and in the vapour phase of the batch reactors. If such analysis method is not supplied by the contractor, it will need to be developed as part of Call-off-2. Typically such method could be based on HPLC, Gas or Ion Chromatography.
2) Test for N-nitrosamines in the liquid phase and in the vapour phase.
3) Test for N-nitramines in the liquid phase and in the vapour phase.
4) Test for carbonyl compounds.

The specific chemical tests are considered necessary to achieve mass balance closure.

The conceptual experimental set-up for the degradation experiments comprises thus a bench top laboratory autoclave with facilities for liquid- and gas phase sampling. A given constant gas pressure is to be assured during the whole test run. To ensure gas-liquid mass transfer a turbine stirrer (or similar) is to be fitted to ensure that the test is run at conditions not limited by mass transfer. This must be documented for the performed tests. Temperature control is to be assured. The autoclave construction has to be as inert as possible towards amine corrosion, thus as one option, the autoclave could be constructed of borosilicate glass and all metal parts could be coated with polytetrafluoroethylene (PTFE; e.g. brand name Teflon).

One possible design for a VLE cell is given below.

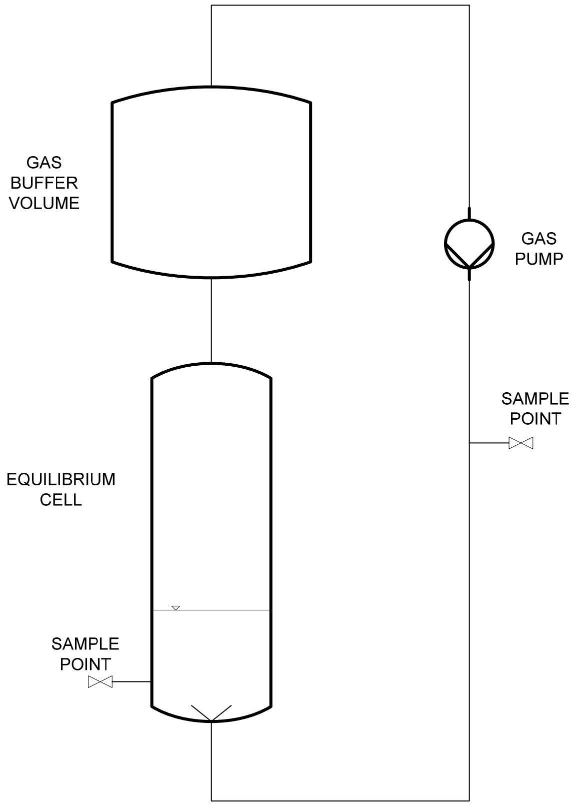

Figure 3.9-1 VLE cell. Closed loop with gas circulation. The temperature is controlled at some level chosen to reflect the appropriate process conditions. This particular flowsheet is based upon a unit that was used to measure absorption equilibria of CO_2 and H_2S in various amine solutions at the University of Alberta in Edmonton. The gas buffer volume is added to minimise the effect of sampling from the system. This volume can in principle be made a part of the equilibrium cell itself.

3.9.5 Recommended experiment conditions.

Experimental conditions shall be worked out according to the described Strategy (Figure 3.5-1), considering feed gas and amine solvent composition, process conditions and other factors considered relevant.

The experimental protocol should comprise testing oxidative degradation in a sufficiently spanned parameter window, comprising experiments with:

1) High/low O_2
2) High/low loading
3) High/low NO_x
4) High/low temperature
5) High/low levels of Fe and/or other defined metals that may be present in the solution

In particular, the experimental conditions will be defined according to the actual operating conditions (to be provided in the documentation defining call-off-2).

3.9.6 Validation of in-process formation and emission of substances

Validation of the output of above work section 4) and choosen experimental conditions in work section 1) to 3) (see 3.9.2) shall be documented by a 6 month trial run in a pilot plant representing the full scale process unit operations and operating conditions.

3.10 Atmospheric gas phase reactions

The Test Protocol for the gas phase reactions is based on the Atmospheric Degradation of Amines (ADA) Protocol for amine screening studies (http://ada.nilu.no/ ; Nielsen at al., 2010).

The gas phase chemistry Experiment Protocol defines a series of photo-oxidation experiments which are suited to elucidate the fate of amines emitted to the atmosphere. The Protocol focuses on the identification of harmful compounds and includes minimum requirements to be met by the experiments.

3.10.1 Specific documentation requirement

1) Documentation of transfer lines between chamber and on-line and off-line instruments and sampling devices
2) Documentation of spectral distribution and intensity of photolysis source.
3) Documentation of the chamber injection system.

3.10.2 Minimum requirements of experiment analysis.

1) All loss processes (surface, particles, gas-phase photo-oxidation) should be quantified and models documented in agreement with practice in international atmospherie chemistry journals. The amount of amine removed by gas-phase photo-oxidation should exceed 100 ppbV.
2) Mass balance closure > 80%. This includes quantification of all products observed.

3.10.3 Specific chemical tests (Target analysis).

1) Test for N-nitrosamines in the gas phase and aerosol. LoD ~10 pptV (10^{-4} of amine removed in gas-phase photo-oxidation).
2) Test for N-nitramines in the gas phase and aerosol. LoD <1 ppbV (10^{-2} of amine removed in gas-phase photo-oxidation).
3) Test for carbonyl compounds.

3.10.4 Recommended experiment conditions.

1) High- NO_x experiment (dry air, high actinic flux): 200-500 ppb amine, 80 ppb NO, 160 ppb NO_2. If possible, continuous addition of NO/NO_2 to keep NO_x constant throughout the experiment.
2) Low- NO_x experiment (dry air, high actinic flux): 200-500 ppb amine, 10 ppb NO, 20 ppb NO_2. If possible, continuous addition of NO/NO_2 to keep NO_x constant throughout the experiment.

3.10.5 Other quantities to be reported

1) Ozone formation potential, $\Delta[O_3]/ \Delta[\text{Amine}]_{\text{reacted}}$.
2) Quantification of the particle production yield using measured particle mass loading.
3) Thermodynamic properties of amine salts (nitrate, sulfate).

Once the kinetics and branching ratios are known for the documented experimental conditions, the atmospheric degradation under (other) relevant conditions can be modeled

3.11 Atmospheric Aqueous phase reactions

3.11.1 Vapour pressures

Vapour pressures of amines used for CO_2 capturing as well as key degradation products such as amides and nitrosamines at standard conditions (298 K) and possibly their temperature dependencies should be provided.

The following main phase transfer parameters of compounds need to be provided or estimated with reference to the estimation method:

1) Gas phase diffusion coefficient
2) Henry's law constant and its temperature dependence
3) The mass accommodation coefficient α ($T = 298$ K)
4) An estimate of the main solution phase sinks as a degradation rate (k_{1st} [s^{-1}])

With the above parameters an uptake coefficients γ can be calculated according to the resistance model introduced by Schwarz (1986) for (a) a cloud case and (b) the deliquescent aerosol for the CAPRAM remote case (Herrmann et al., 2005; Tilgner and Herrmann, 2010), see http://projects.tropos.de/capram/. Knowing the partitioning of amines and their degradation products in the atmospheric multiphase system supports the indentification of processes that should be targeted for experimental investigations on aqueous phase reactions. As stated in the report the amine degradation processes in the gas and aqueous phase can be quite different which can result in completely different products and lifetimes of the compounds. Therefore, an exact characterization of the phase transfer parameter of amines helps to prioritize if degradation processes in one of the phases can be neglected for certain compounds. For example, studying aqueous phase processes of an compound mainly present in the gas phase is not much of help if one wants to describe the atmospheric fate of this compound.

3.11.2 Atmospheric aqueous phase reactions

1) The main degradation products of the compound in atmospheric aqueous particles with relative yields above 1 % need to be identified by either adequate literature or conducted aqueous phase oxidation studies applying a bulk reactor for the generation of OH in solution with sampling and product studies.
2) Besides the main degradation products following H-abstraction by OH, special attention needs to be paid to formation of nitrosoamines and nitramines possibly formed by aqueous phase reactions of the amines in question with nitrite.
3) In case nitrosoamines or nitramines are identified, their main sink reaction efficiency needs to be quantified, i.e. the degradation by OH and the photolytic lifetime in solution for Mongstad conditions. Proper referencing to studies described in the literature needs to be given or laboratory testing experiments need to be performed.

3.11.3 Specific documentation requirements

As for the gas phase processes described in section 3.10.1.

3.11.4 Minimum requirements of experimental analysis

Quantification for aqueous phase loss processes with relative loss contributions of the mother compound above 1 %. At least 10 μmol l^{-1} of amine should be removed by OH oxidation or other sink reaction applicable. A mass closure better than 80 % should be achieved.

3.11.5 Specific chemical tests - procedure for amines out of aqueous solutions

Amine analysis with a derivatization reagent 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate and HPLC/ESI-MS and UV. LODs between 0.6 µM for methylamine and 1.3 µM for dimethylamine in the solution (Müller et al., 2009).

3.11.6 Recommended experimental conditions

Bulk reactor with 100 ml volume or photolysis cuvette and 10^{-4} mol l^{-1} amine concentration. Total OH generation of at least 10^{-5} mol l^{-1} over experiment time by continuous photolysis, pulsed photolysis of adequate precursors, e.g. H_2O_2.. pH = 4.5 for cloud and pH = 1 for fresh aerosol particle conditions. Degradation of at least 10 µmol l^{-1} of amine.
Test of the effects of added nitrite (a) in the dark, (b) photolysis under natural photolysis conditions ($\lambda > 290$ nm).
Test of nitrosamine and nitramine lifetimes with regard to (a) OH degradation and (b) photolysis under natural photolysis condition ($\lambda > 290$ nm).

3.11.7 Output

1) Calculation of uptake coefficients and mass accommodation coefficients in order to describe the partitioning of amines (treated in the project) and degradation products of particular interest such as nitrosamines.
2) Measurements on the reactivity and photolysis processes of amines and degradation products (in particular nitrosamines) in aqueous solution. Experiments will deliver kinetic data of important degradation processes (radical reactions and photolysis processes) as a function of atmospheric parameters such as the pH, the temperature and the ionic strength. These data are required for lifetime calculations and help to evaluate the risk of exposure to amines and nitrosamines.
3) Characterization of amine degradation products by product measurements using HPLC-MS as long as no adequate literature is available. These measurements helps to verify the theoretical degradation schemes and gives some information on the yields and distribution of the reaction products.

3.12 Uncertainties and limitations

Reports shall include analytical uncertainties as well as uncertainties in estimates and models. Limitations of the equipment, analyses, and methods used shall be evaluated when relevant for the Test Protocol.

Any modifications or deviations from the Test Protocol shall be explained.

3.13 Conclusions and recommendations

Reports shall make conclusions and recommendations. Recommendation shall include proposals for improvement of the Test Protocol.

If the results are such that it is difficult or impossible to make conclusions explanation shall be given.

3.14 Output

The output from the activities shall be combined in a report stating:

- An estimate of the emission of compounds with the flue gas.
- An estimate of aerosol emission, kg/hr and droplet size distribution based on vender estimate.
- Necessary parameters and reaction schemes to model the chemical reactions in the atmospheric gas and aqueous phase, as an input to dispersion modelling.
- A risk evaluation
- Any proposals for improvement of the Test Protocol.

3.15 Risk

3.15.1 Development time available

The short time available is a significant risk. If it is decided to have a 6 months validation period, a best guess estimate must be used for several compounds and parameters. This will reduce the quality of the output of the protocol. This will increase the risk.

3.15.2 Emission reduction technology

An ERT with bad performance is a significant risk, and can be considered as a "worst case". The obvious mitigation is to have a properly designed, efficient, reliable and properly operated emission reduction technology. We strongly recommend that design and performance of ERT are validated at pilot plant scale or preferably full scale.

3.15.3 Mass transfer

A signifikant risk element is parameters for the mass transfer from gas phase to aqueous phase. As stated in the literature review report such parameters (gas phase diffusion coefficient, Henry's law constant, and the mass accommodation coefficient) are missing for almost all compounds of interest. Mitigating action is to experimentally determine these parameters or estimate these parameters based on models or similar compounds where available. Realistically the experimental determination of parameters would take several years due to the number of compounds. Also some compounds would need to be synthesised before such measurements. There will also the HSE risk in synthesising and handling some of these compounds which are harmful.

We suggest that such work shall be initiated by the CCM project for a selected set of compounds. The selection of compounds to be investigated should be based on the H&E TQP Amine 4 call off 1 reports, as well as what is known of which compounds are considered to be most harmful. The most important mass transfer data to be determined are those of the amine in question and the corresponding nitrosamine (if stable) and nitramine. This can be done for the case-study reference amine (MEA) within the time-frame of "a call-off 2 project".

In the case that gas-liquid mass transfer data are not available, a worst case model can assume that there are no mass transfer limitations.

3.15.4 Chemical reaction and dispersion model

A significant risk element is the ability to correctly model chemical reactions in the aqueous phase, in combination with dispersion models. This is partly linked to the risk above, but also to the lack of knowledge about which compounds actually are formed and lack of chemical reaction kinetic data.

Mitigating actions with regard to determine the necessary parameters are listed as research recommendations in the WP2 report.

We suggest that such work shall be initiated by the CCM project for a selected set of compounds. The selection of compounds to be investigated should be based on the H&E TQP Amine 4 call off 1 reports, as well as what is known of which compounds are considered to be most harmful.The state of art of dispersion models that include chemical reactions should be improved.

4. PLAN FOR DEVELOPMENT AND VERIFICATION

It is proposed that the Test Protocol should be developed and validated using MEA. MEA technology is considered the base case for amine solvent processes. The literature reviews have shown that more is known about the reactions of MEA than the other amine solvents proposed for CC processes. The results from the verification activities during the development of the Test Protocol can by using MEA better be compared to results in the scientific literature.

The development of the Test Protocol shall be based on the ISO 9001 model:

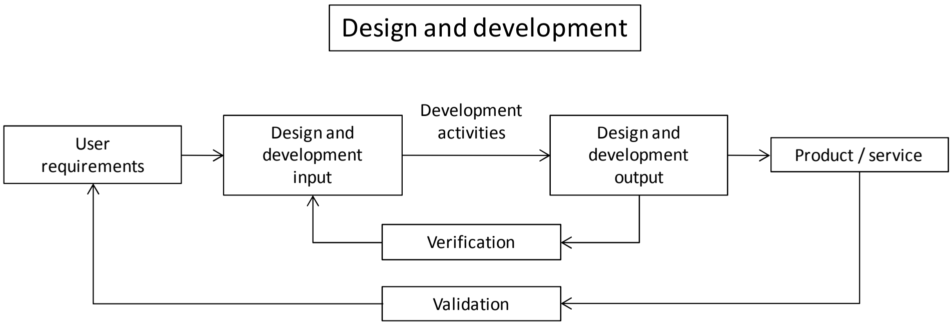

Figure 4.1 Simplified diagram for verification and validation activities (adapted from Pronorm, 2003)

The Test Protocol as described in this report shall be used as the starting point.

The development is an iterative process. In the case where verification shows that the equipment and/or methods used do not fully meet the user requirements; modifications and retesting, or other corrective actions may be necessary.

Output from one activity will be input to another activity. Special attention shall be given to the interaction between the main activities:

- Compounds emitted with the flue gas is input to the atmospheric gas and aqueous phases
- There is a phase transfer between the gas and aqueous phases in the atmosphere.

Compounds that are not described in the literature reviews may be detected during testing. One must ensure that such compounds are considered both with regard to gas and aqueous atmospheric phases.

The general scheme to be followed is:

- Verification of equipment and instruments
- Verification of sampling and analytical methods
- Testing at relevant conditions
- Analysis of results, verification of results against the input criteria.

The ”Plan-Do-Check-Act” methodology as described in the ISO 9001 standard will be used.

Note: The equipment to be used and chemical analysis methods to be used are not outlined in more detail here as these are the scope of a separate project (cfr. Section 3.8).Results from the ADA project will also be used as a basis for the detailed plans. Together the University of Oslo, *Leibniz-Institut für Troposphärenforschung, Telemark University College, Norner Innovation, and Tel-Tek have appropriate equipment and instruments, or can have access to such through established networks.*

The final Test Protocol may deviate somehow from the solution proposed in this text since it will be the result of an iterative optimisation process. Furthermore, it has to be kept in mind that if the analytical methods supplied by the CCM project do not meet the specific needs of the current Test Protocol these will have to be developed as part of the further work scope as well.

We consider that 6 months is a minimum time needed for validation of the test protocol, and that another 6 months is needed for the optimisation of the test protocol.

The state of the art knowledge about the reactions of amines and compounds formed from them is unfortunately at a stage where this time is necessary. If is is decided that 6 months is the time available for validation of the Test Protocol, we consider that an additional 6 months is necessary for optimisation and for risk mitigation. This may be a parallel activity to the use of the protocol on amine solvents offered by venders, and will reduce risk by the possibility to ask the vender for additional tests.

There shall be a final review and evaluation of all verification activities to validate the Test Protocol, and the use of the Protocol for amine solvents.

5. LITERATURE

Herrmann, H., Tilgner, A., Barzaghi, P., Majdik, Z., Gligorovski, S., Poulain, L., Monod, A., 2005. Towards a more detailed description of tropospheric aqueous phase organic chemistry: CAPRAM 3.0. Atmospheric Environment. 39, 4351-4363.

Müller, C., Iinuma, Y., Karstensen, J., van Pinxteren, D., Lehmann, S., Gnauk, T., Herrmann, H., 2009. Seasonal variation of aliphatic amines in marine sub-micrometer particles at the Cape Verde islands. Atmospheric Chemistry and Physics **9**, 9587-9597.

Nielsen, C. J.; D'Anna, B.; Dye, C.; George, C.; Graus, M.; Hansel, A.; Karl, M.; King, S.; Musabila, M.; Müller, M.; Schmiedbauer, N.; Stenstrøm, Y.; Wisthaler, A. (2010). Atmospheric Degradation of Amines (ADA). Summary Report: Gas phase photo-oxidation of 2-aminoethanol (MEA), NILU.

Pitts, J. N., Grosjean, D., Vancauwenberghe, K., Schmid, J. P., Fitz, D. R., 1978. Photo-Oxidation of Aliphatic-Amines under Simulated Atmospheric Conditions - Formation of Nitrosamines, Nitramines, Amides, and Photo-Chemical Oxidant. Environmental Science & Technology **12**, 946-953.

Pronorm, 2003. NS-EN ISO 9001 for små virksomheter. ISBN 82-7202-529-9.
(*note: this is a guidance and not a standard*)

Schwartz, S. E., 1986. Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds, NATO ASI Series Vol. G6.

Tilgner, A. and Herrmann, H., 2010: Radical-driven carbonyl-to-acid conversion and acid degradation in tropospheric aqueous systems studied by CAPRAM. Atmospheric Environment, in press, doi:10.1016/j.atmosenv.2010.07.050.