CO_2 Capture Mongstad - Project B - Theoretical evaluation of the potential to form and emit harmful compounds

Task 3: Test Protocol

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EXECUTIVE SUMMARY

An estimate of the environmental impact of PCC plant operations, especially the atmospheric emissions or “slip” of the amine or amine formulation and any associated degradation products, together with the propensity of any slipped chemicals to react in the atmosphere, is required prior to deployment. This report describes a test Protocol with a series of activities aimed at the evaluation of proprietary solvents for use in PCC processes.

The Protocol proposed in this document is intended to identify the degradation products of solvents or formulations which are potential volatile pollutants, as well as chemicals that could react further with oxides of nitrogen, either in the atmosphere or in the PCC liquor, to produce nitrosamines, nitrosamides and/or nitramines. These are harmful chemicals which could be released to the environment in a number of ways during normal PCC plant operations

The proposed Protocol is designed for testing aqueous amine mixtures as well as aqueous formulations with proprietary additives. It is multi-tiered, with steps of differing chemical complexity, allowing early identification of potential emission of harmful components. It relies on both high- and low-end spectroscopic/chromatographic methods, as well as specialised PCC research equipment, for the detection and identification of:

N-containing products which can be considered toxicants

major degradation products with the potential to react further with the capture amine to produce pollutants or toxicants, and

compounds with the potential to be emitted in large quantities and/or which may form N-containing toxicants in the atmosphere directly or via further reactions

Standardised tests, benchmarked against a standard amine or formulation (e.g. 30 % MEA), will provide information concerning:

i. the *in-situ* plant degradation chemistry of the amine under typical flue-gas scrubbing conditions,

ii. the rates of formation of specific degradation products in the plant liquor, in addition to

iii. the atmospheric chemistry of the suite of compounds produced during CO_2 capture

A plan for the validation of the Protocol is also provided. The report also provides a description of two facilities, i.e. the smog chamber and a PCC pilot plant considered to be important infrastructure for the final evaluation of proprietary solvents.

1. INTRODUCTION

Sour- or acid-gas removal technologies for natural and synthetic gas stream processing are proven at a small to medium commercial scale (Kohl and Nielsen, 1997). In order to mitigate anthropogenic CO_2 emissions from large point sources such as fossil fuel power stations, the scale-up of technology for the capture of CO_2 from flue gas streams has been proposed. Given the widespread use of fossil fuels for electricity generation, particularly in large emerging economies, the success of PCC is considered critical to reduce the environmental impact of high atmospheric CO_2 levels on a global scale.

The chemical process behind PCC involves reversible chemistry between an amine in the aqueous phase and dissolved CO_2; the reasonable chemical "selectivity" of the capture reaction ensures the scrubbed flue gas that is eventually exhausted to the atmosphere is CO_2-lean and consists predominantly of environmentally benign gases of high atmospheric abundance. PCC technology is also 'switch on/switch off', and can be adapted to capture emissions according to any operational or legislated requirements.

It has long been recognised that reactions between other flue gas components and the solvent amine or additives can also occur, and ultimately inhibit the solvent capture performance to the extent that the solvent needs replacing; the solvent is a plant consumable. Some of these reactions include heat-stable salt formation through conversion of SO_x and NO_x to sulphate and nitrate anions (Rooney, Bacon and DuPart, 1996-7), which can form ion complexes with amines; oxidative degradation which results in the formation of ammonia and organic acids, as well as volatile aldehydes (Chi and Rochelle, 2002; Rooney *et al*, 1998) and thermal degradation that results in the formation of N-formyl, N-acetyl and amide species (Strazisar *et al*, 2003). An unexpected consequence of NO_x (or nitrogen oxides) in the flue gas has recently been discovered i.e. the formation of aqueous nitrite or other aqueous oxides of nitrogen which lead to the formation of nitrosamines (Jackson *et al*, 2010; Jackson and Attalla, 2010; Pedersen *et al*, 2010). The formation of nitrosamines in PCC process plants has been previously reported (Strazisar *et al*, 2003; Pedersen *et al*, 2010). The chemiluminescent method used in establishing nitrosamine presence *in one instance* was a functional group test prone to interference. Mass spectrometry detection (e.g. Jackson and Attalla (2010)) is not ambiguous and nitrosamine formation for a common secondary amine solvent (aqueous piperazine) at high pH in the presence of O_2, CO_2 and NO_x has been demonstrated.

A method for assessing the H&E properties of solvent formulations for PCC application using a blind-testing protocol is needed. There is an associated need to identify terminal and/or persistent atmospheric degradation products in the event that components of the solvent formulation are released to the atmosphere, either within droplets or as volatile chemical degradation products. This aspect is described in detail in the report Project B Task 2. Approaches developed as part of this task are integrated into the Protocol proposed below. Estimates of solvent release can be obtained using process engineering models or estimated using relevant literature (e.g. see Veltman *et al*, 2010); These data are captured in the report Project B Task 1. The process model output is inextricably linked to the availability of relevant and accurate

thermodynamic parameters for the solvent and pollutant molecules of interest. In addition, a well-developed understanding of the process chemistry is required, which may not be available.

2. SCOPE

This report addresses the scope of work described by the client (CCM) for Project B Task 3:

"*A test protocol shall be proposed to enable a direct evaluation of proprietary solvents. The test protocol shall describe a set of activities needed to identify and quantify the compounds emitted with the cleaned flue gas or formed post-emission when a given solvent is used in a full-scale capture plant. The design and operating conditions of the testing facility or facilities that will be used as part of this protocol must be described. A plan for the development and verification of the protocol shall be presented.*

Separate studies will be undertaken to develop methods for chemical analysis of potentially harmful compounds, such as nitrosamines, nitramines and alkylamines. These methods can be applied by the test protocol provider, and will be used by the company for verification of test protocol results. The test protocol must define the chemical analysis strategy and needs of the test protocol. Design and use of available sampling points must be described. (Note that a full description of sampling methods and analytical procedures is presented in PROJECT A Task 1.)

The experimental design and set-up for this test protocol should enable gas-phase (emission) sampling for both chemical analysis and toxicity testing."

3. OVERVIEW OF TEST PROTOCOL

3.1 General

The outcomes from the process chemistry evaluation (Project B Task 1) and atmospheric degradation study (Project B Task 2) have highlighted deficiencies in our current understanding of the potential for solvent-associated pollutants, particularly nitrosamines and their rates of formation. Project B Task 2 has also highlighted the possibility of secondary organic aerosol formation following the release of amines to the atmosphere. These points have been carefully considered during the preparation of the following procedure for testing amine solvents.

A testing protocol should rely on:

- simple laboratory procedures using common and inexpensive laboratory equipment in the first stages,
- more complex, purpose-built equipment, high-end spectroscopic instrumentation and numerical modelling in the final stages.

The focus of the Protocol should be skewed towards condensed-phase PCC liquor chemistry because:

- any chemistry in the liquid droplets entrained into exhausted gases will reflect the composition of the PCC solvent and wash water, and the chemistry which occurs in these droplets will be representative of solution phase chemistry
- any plant losses (spills etc.) will also reflect the composition of the liquor and wash water, and
- a crucial aspect of PCC solvents is their relatively low vapour pressures making it extremely difficult to study gas phase reactions.

However given that H&E issues are transferred primarily through the atmosphere, the Protocol should include an analysis of the anticipated fate of emitted solvent components and reaction products at an early stage.

The Protocol is also intended to provide feed-back to vendors to allow for improvements or modifications to be made at an early stage.

3.2 Outline of test protocol

In determining the potential environmental impacts from PCC emissions from the process, it is critical to:

- establish the chemical composition of the emissions

- establish the emission rates
- establish the potential environmental impact of each significant species

A multi-tiered five step solvent testing protocol is proposed involving the following steps:

Steps 1 and 2

Steps 1 and 2 of this Protocol identify:

a) any solvent components that could produce harmful components in particular nitrosamines and nitramines or volatile molecules such as aldehydes that are regulated by air quality standards, and

b) the rates of reaction of solvent components with nitrite *or* dissolved oxides of nitrogen *or* thermal/oxidative degradation products which could produce nitramines or nitrosamines

The test conditions for Steps 1 and 2 of the Protocol can be performed within a very short time frame. This information suggests these tests are the best available measure for the early and rapid identification of toxicant chemicals such as nitrosamines, ammonia and small, volatile aldehydes which may be produced at the pilot or full-scale plant level. Where appropriate use should be made of available results from pilot plant trials, provided the conditions for the trials are documented.

Key information collected from these steps:

- places the testing body in a position to implement adequate H&E handling precautions for further protocol test steps, or prior to pilot-scale testing
- provides an early feedback mechanism for the solvent vendor,

Note: The emphasis of all Protocol steps is testing within a controlled environment, with the safety of plant- and test-procedure personnel given the highest priority.

Step 3

Step 3 of the Protocol relies on more complex, purpose-built solvent degradation equipment together with more sophisticated spectroscopic instrumentation. The purpose of test Step 3 is:

- the closest possible replication of realistic PCC capture conditions for the solvent after considered input from the solvent vendor, and
- the unambiguous identification of potential pollutants/toxicants that will be generated *over longer time periods* during operations with the vendor's solvent.

Repeated solvent absorption and regeneration (cycling) under conditions specified by the solvent vendor is implemented in a laboratory-scale device representative of a scaled PCC plant. Device parameters must be independently adjustable to replicate the scaled PCC plant as closely as possible. As a minimum, the following parameters need to be controlled variables:

1. synthetic flue gas flow rate

2. synthetic flue gas composition

3. capture solvent flow rate

4. capture solvent absorption temperature

5. capture solvent regeneration temperature

6. mass-flow meters for mass-balance requirements

The variance of each parameter needs to be captured during experimentation for quality control purposes with the use of an appropriate data-logging system. All set-points reflect the vendor's specifications within the apparatus' tolerances. Consideration for sampling points includes:

1. adapters for the insertion of gas-sampling cartridges (acid/derivative or preservative impregnated) on both the absorption and desorption sides of the apparatus**

2. adapters or switches for the incorporation of liquid impingers on exhaust gas lines

3. direct PCC liquor*** sampling ports

4. direct wash-water sampling ports

*** referred to hereafter as the laboratory gas sample; *** referred to hereafter as the laboratory liquid sample*

Laboratory gas- and liquid samples are acquired at regular intervals during this test procedure. Test samples are sent for analysis using techniques such as high performance liquid chromatography – mass spectrometry (HPLC-MS), gas chromatography – mass spectrometry (GC-MS), ion chromatography (IC), ultra-violet fluorescence spectroscopy (UVF), ultra-violet-visible absorbance spectroscopy (UV-VIS), or chemi-luminescence analysis.

The information captured during execution of Steps 1 through 3 are then pooled for critical assessment in Step 4.

Step 4

Pollutants including solvent components and degradation products are identified and a survey of the literature is undertaken to uncover:

- regulatory requirements governing environmental release pertinent to the vendor's location,

- available thermodynamic data for input into mass-balance process modelling.

The mass-balance modelling will provide emission rates. The emission rates will depend on the process details available for model input.This step is limited by the parameters/databases available for model input. As such, any output from this modelling will need careful scrutiny. We recommend the compilation of a thermodynamics database for PCC and solvent degradation specifically for this purpose. Modelling scenarios with an appropriate data set will provide estimates of carry-over and droplet emissions from operational PCC plant.

Note: It is expected that published information covering many of the chemicals identified in test Steps 1 through 3 will be scarce; for this reason, ecotoxicity testing at this stage of the Protocol is justified and considered crucial for informed vendor feedback. Toxicity testing information is deemed integral at the final reporting stage as it is a logical next step to obtain this information after emission rates have been determined for a full-scale PCC operation using the process modelling. This additional information provides the vendor with a report containing all data required for informed decision making, particularly in relation to regulations and any potential liabilities.
Although the toxicity testing work can be undertaken separately, it is still required as part of the solvent evaluation.

The potential impact of non-reactive species can be assessed using an appropriate dispersion model with dry and wet deposition algorithms. The spatial and temporal profiles of pollutant concentrations can also be obtained for risk assessment evaluations.

Additional research is necessary for reactive gaseous species such as small amines which are considered volatile organic compounds (VOC's). The detailed review of atmospheric chemistry Project B Task 2 has provided a summary of the current understanding of these processes and two complementary scenarios have been proposed:

- an Incremental Reactivity Scale for amine interactions with NO_x to be compiled, and

- a lumped chemical reaction model for inclusion in air quality models to be developed

The overall strategy is that basic information on photochemical reactions can be provided by smog chamber and chemical modelling studies and the synthesis of these two approaches used to develop simplified models for use in air quality models.

Due to the low volatilities of amines used in CO_2 capture (Piperidine, AMP and MEA are exceptions), careful appraisal of the likely outcome of any smog chamber studies is needed. Small, volatile toxicants for which there is no available atmospheric data can be readily examined using this technology. Smog chamber studies can also provide information concerning formation of secondary aerosols and enhanced droplet formation.

The environmental fate of many of the pollutants will be unknown. Knowledge gaps are identified during this step. *Ab initio* computational chemistry investigations can be used at this point of the solvent assessment process for identifying:

- terminal atmospheric chemical products and atmospheric degradation rates

- the photolytic stability of pollutants containing –NO or –NO_2 functional groups.

Step 5

This is the final step of the Protocol. The results of the test procedures for the solvent are provided to the vendor. Sufficient information is provided for the vendor to make an informed decision regarding either:

1. re-formulation of the solvent, or

2. proceeding to pilot-scale trials

The results of the Protocol for the vendor's solvent are compared with results obtained for a generic solvent such as 30 wt % MEA. 30 % MEA is chosen as a benchmark. The rates of emission of chemical components identified in Steps 1 through 3 are provided to the vendor, based on mass-balance modelling (Step 4). The fate of these chemicals in the atmosphere is also detailed in the report, based on the literature survey and air quality modelling from Step 4. The environmental impact of plant emissions is provided, based on air quality standards pertaining to the release of volatiles identified in Steps 1 through 3. In some cases, air quality regulations will not be available for some pollutants. In these cases guidance will come from literature searches of health and safety databases. In addition, ecotoxicity testing data will be assessed against relevant environmental health and regulations. Pilot trials will be proposed and where possible integrated with general performance test of the solvent.

3.3 Summary of testing protocol

A descriptive summary of the Protocol appears in Table 1.

Table 1. Summary of the Test Protocol Steps

Protocol Step	Objective
1	DETERMINE THE PROPENSITY OF AN AMINE FORMULATION TO FORM N-NITROSATED COMPOUNDS
2	TO GENERATE DELETERIOUS SOLVENT DEGRADATION AND CAPTURE BY-PRODUCT MOLECULES IN A SHORT TIME FRAME (E.G. FEW WEEKS) USING ACCELERATED SOLVENT DEGRADATION TECHNIQUES IN A SAFE/CONTROLLED ENVIRONMENT.
3	CARRY OUT LABORATORY EXPERIMENTS UNDER SIMULATED OPERATIONAL CONDITIONS TO BETTER UNDERSTAND THE PROCESS CHEMISTRY AND TO IDENTIFY AND QUANTIFY HARMFUL COMPOUNDS.
4	CLASSIFY THE IDENTIFIED COMPONENTS AS *REACTIVE* AND *NON REACTIVE* COMPOUNDS DETERMINE THE EMISSION RATES OF THE IDENTIFIED HARMFUL COMPONENTS UNDER PCC PROCESS CONDITIONS CARRY OUT PLUME DISPERSION MODELLING FOR *NON REACTIVE* SPECIES FOR REACTIVE SPECIES CLASSIFY THE COMPOUNDS AS EITHER THOSE WITH *KNOWN* ATMOSPHERIC CHEMISTRY OR THOSE WITH *UNKNOWN* ATMOSPHERIC CHEMISTRY FOR SPECIES WITH *UNKNOWN* ATMOSPHERIC CHEMISTRY, THE USE OF (I) QUANTUM CHEMICAL METHODS WILL BE USED TO INVESTIGATE THE FATE OF NOVEL POLLUTANTS, AND (II) 2D OR 3D AIR QUALITY MODELS WILL PREDICT THE SPATIAL AND TEMPORAL CONCENTRATIONS OF MAJOR POLLUTANTS OF CONCERNS OVER THE SELECTED DOMAIN. ELUCIDATE THE ATMOSPHERIC CHEMISTRY FOR SPECIES WITH *UNKNOWN* CHEMISTRY USING SMOG CHAMBER EXPERIMENTS IF NECESSARY. ECOTOXICITY TESTING AND EVALUATION FOR SPECIES WITH *UNKNOWN* ATMOSOPHERIC CHEMISTRY
5	REPORTING OF TEST RESULTS TO THE VENDOR A. REFORMULATION B. PILOT PLANT TRIALS

4. DEVELOPMENT AND VALIDATION OF THE PROTOCOL

4.1 General

The methods described in:

- Step 1
- Step 2 part 2

were developed in-house. These methods have been tested within CSIRO laboratories, but have not been tested independently.

The method described in:

- Step 2 part 1

(the accelerated degradation of alkanolamines at high pressure and at temperatures exceeding typical stripping/regeneration temperatures) is used by a number of leading PCC research laboratories, including CSIRO, and many results applying this technique can be found in the open literature. These experiments have been performed a number of times for individual alkanolamines, and also across a broad suite of different alkanolamine classes (eg. primary, secondary and tertiary). There are no *validated* procedures for the accelerated degradation of alkanolamines *per se*.

The Protocol proposed in this document is based on the broad PCC experience of PhD-level chemists and chemical engineers who have weighed their own laboratory expertise against information discerned during an extensive review of the open literature.

4.2 Special cases

In the event that an unforeseen interference is encountered for Protocol Step 1 - the UV-VIS procedure - the details of an alternative method are presented in Appendix B. The method presented in Appendix B method is based on chemi-luminescent detection. There are several variants of this method in the literature, and the method in Appendix B is based on the one reported by Drescher and Frank (1978).

As stated previously, there is a strong possibility thermodynamic and kinetic data necessary for the determination of emission rates may not be available, and will need to be computed using computational chemistry or gathered through dedicated experiments. The atmospheric fate of unusual volatile molecules may also need to be modelled using this approach, and/or investigated experimentally using a smog chamber.

4.3 Validation of the Protocol

In the first instance the Protocol will be evaluated by running a selected number of solvents, whose chemistry is well known, through Steps 1 to 3. This will provide an assessment of how well the Protocol performs for known solvents. The process will require the use of well established methods for determining a number of expected compounds. In particular it is anticipated that, for Steps 2 and 3, the analyses will be carried out using the following standard methods;

1. NIOSH 2522, Issue 2. Volatile nitrosamine analysis using GC-TEA from solid sorbent Thermosorb/N gas cartridges*

2. USEPA method 521. Determination of nitrosamines in drinking water by solid phase extraction and large-volume injection capillary column and CI-GC-MS/MS

3. USEPA method 8070A. Determination of nitrosamines in municipal waste-waters using GC-NPD.

4. NIOSH 2016, Issue 2. Formaldehyde analysis using 2,4-DNPH impregnated gas cartridges with HPLC-UV detection*

5. NIOSH 2010, Issue 2. Volatile amine analysis using acid-impregnated gas cartridges and GC-FID

6. NIOSH 3509, Issue 2. Analysis of aminoalcohols using a liquid impinger and ion chromatography.

** Note: methods can be adapted for more than one analyte*

Note there are no validated methods for the non-volatile nitrosamines. Methods appear in the literature for N-nitrosodiethanolamine (NDELA) and an in-house method for the analysis of N-nitrosopiperazine has been developed (see Appendix A).

As Steps 1 to 3 have been developed based on the detailed chemistry of known solvents it is anticipated that the data obtained will confirm the usefulness of the Protocol.

As Step 4 concerns the environmental impact of the emissions, it relies on a number of well established methods and models for predicting such impact. In particular the emission rates will have to be calculated from an appropriate model of the PCC process. In addition a distinction must be drawn between data, methods and models that are available and widely used (eg process modelling, air quality modelling, toxicity assessment) and situations where the base data simply do not exist (eg atmospheric fate of many of the chemical compounds of interest). In the former case standard approaches are applicable while in the latter, research will be required. This research will draw upon smog chamber experiments, detailed and lumped chemical kinetic modelling as well as quantum chemistry.

Also, validation of the Protocol will require field based measurements under pilot plant conditions to provide full confidence in the Protocol performance (Step 5).

It is anticipated that the validation plan involving Steps 1 to 3 can be accommodated within a time period of 6 months.

The timeframe for Step 4 of the Protocol must be considered in two parts.

- The modelling of the PCC process and determination of emission rates as well as plume dispersion modelling should be able to be achieved within a short time frame (1 month) depending on the availability of meteorological data.

- The timeframe for the any necessary research program involving smog chamber investigation, chemical and air quality modelling will depend strongly on the level of information required and is difficult to estimate at this stage.

The ultimate deployment of the Protocol in industry will require availability of independent laboratories or contractors with the necessary key capabilities. This will ultimately determine the exact timeframe for method validation.

5. PROTOCOL DETAILS: STEP ONE

5.1 General

This is a simple chemical test, and aside from the reagent chemicals, it only requires access to a UV-VIS spectrometer. The test is used to establish the presence of secondary nitrogen centres (either as capture amines, promoters or inhibitors in the form of amides or amines) in the formulation, via derivatisation to N-nitrosamines which absorb UV radiation at the wavelengths specified.

5.2 Purpose

To determine the propensity of an amine formulation to form nitrosamine/nitramine by-products and their stability to ultra-violet light. Table 2 is an abbreviated description of the aim of the Step 1.

Table 2. Compounds analysed in Step 1.

Step	Degradation Products Tested For
1	Group test for nitrosamines

5.3 Experimental Procedure

Add 5 ml of 2 M $NaNO_2$ to 10 ml of test sample in a 20 ml amber vial (or vial wrapped in Al foil). Add conc. HNO_3 dropwise to adjust the solution pH to 5. If the pH falls below 5, discard the contents (with due consideration to the environment), repeat the nitrite addition step, and adjust the pH using *dilute* HNO_3 to pH 5. Heat the resulting mixture in a waterbath (80-90 °C) for 1 hour. Leave the solution to cool in a fumehood.

Once cooled, adjust the pH value to 10 dropwise using conc. KOH solution. Transfer the resulting mixture to a 50 ml separating funnel and extract with 3 x 20 ml aliquots of dichloromethane (DCM). Retain the organic layer, (discard the aqueous layer), and evaporate under a stream of N_2 gas to a volume of 5 ml. Anhydrous Na_2SO_4 (baked in an oven for 6 hrs at 150 °C and cooled to room temperature) can be used to dry the DCM at this step.

Transfer the organic layer (5 ml) to a clean 50 ml separating funnel. Extract with 3 x 10 ml aliquots of ultra-pure charcoal-filtered (R > 18 MΩ) water. Discard the organic layer (with due consideration to the environment), and evaporate the aqueous layer under N_2 to 20 ml.

UV-visible spectroscopy measurements: quartz cells (transparent to 190 nm) are required. Measurement range: 200-400 nm. Add enough aqueous mixture to ensure the UV cell is filled.

5.4 Analytical Procedure

The analytical procedure assesses the photo-susceptibility of any absorbing species (eg. nitrosamines) to UV irradiation. UV irradiation destroys some nitrosamines (Volmer *et al*, 1996; Cheng *et al*, 2006), but results vary according to the nitrosamine structure i.e. it is an intrinsic molecular property. UV photolysis is widely used to disinfect waters contaminated with nitrosamines (Hartmetz and Slemrova, 1980; Mhlongo *et al*, 2009)**.**

A schematic diagram of the apparatus required for this test procedure is presented in Figure 1. The apparatus consists of a variable-speed liquid pump – preferably dosing/peristaltic type; a light-tight, fan- or water-cooled box which houses one or several commercially available (eg 15 W) mercury discharge bulbs (λ = 254 nm); an appropriate length of UV-transparent tubing, either quartz or teflon. The tubing must be positioned such that there is a clear line-of-sight to the light source; tubing overlap could obscure the solution from UV radiation. Hereafter, this equipment is referred to as the reaction chamber. The procedure recommended is as follows: the UV-VIS absorbance of a test sample is measured (200-400 nm, see Section 7.3) just prior to UV exposure. A suitable volume of the sample is then pumped at a fixed speed through the tubing/light proof housing and subjected to UV irradiation. It is then collected at the reactor exit point (indicated in Figure 1). UV-VIS analysis is performed on the solution after elution. The difference in absorbance 'before' and 'after' photolysis reveals the extent to which any nitrosamine is reactive towards UV light. If the internal diameter of the tubing, the pump speed and power output of the lamps across the UV spectrum are accurately known, the UV dose required to photolyse the nitrosamines can be determined (J L $mol^{-1}s^{-1}$).

5.5 Discussion

Most nitrosamines exhibit two absorption bands in UV region due to n-π* and π-π* transitions (Fiz *et al*, 1993). The long wavelength transition usually has a lower molar extinction coefficient than the short wavelength transition, and can be utilised to quantify higher levels of nitrosamines. The shorter wavelength transition can be used to quantify lower levels. Test sample dilution may be necessary. The nitrite ion (NO_2^-) also absorbs in this region of the UV (354 nm and 210 nm)- see Figure 2. Laboratory tests conducted at CSIRO have revealed that the extraction step eliminates > 95 % of unreacted nitrite. The simplicity of UV analysis, and the ubiquity of these spectrometers in the field, makes this an attractive approach relative to chemi-luminescence (Drescher and Frank, 1978; Kulshrestha *et al*, 2010), which involves more specialised equipment. Both UV absorbance and chemiluminescence approaches rely on the nitrite ion partitioning almost exclusively in the organic layer (trace amounts of water can give rise to large interferences). Given the similarity of both analyses (with the exception of the greater simplicity of UV-VIS analysis), an alternative method to UV-VIS which utilises chemiluminescence (liberated NO gas detection) is presented in Appendix B.

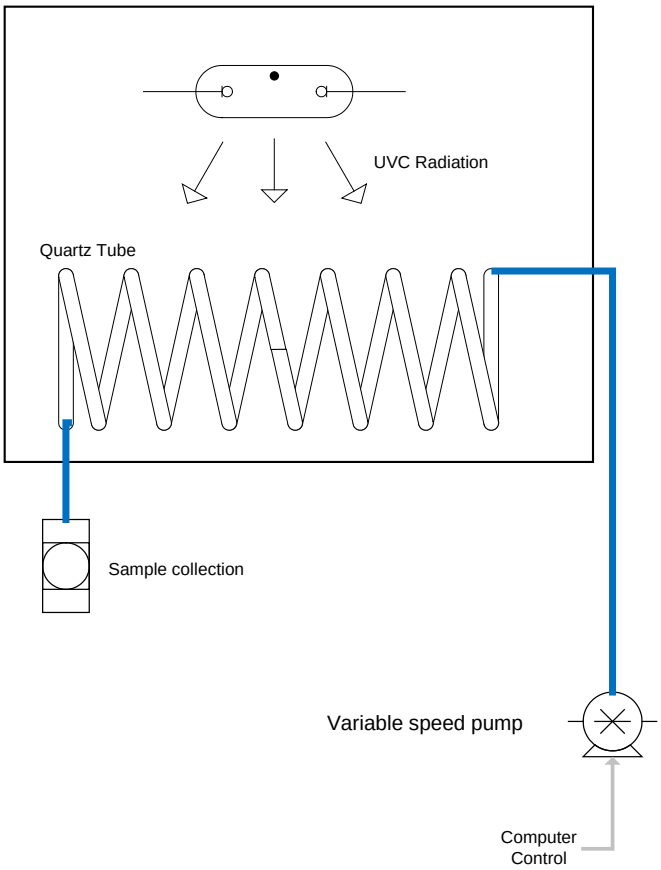

Figure 1. A typical UV-irradiation reaction chamber.

Bicarbonate and amines (with the probable exception of aromatics/aniline derivatives) are UV silent in the 200-400 nm region, whereas carbamates have very low extinction coefficients (verified in our laboratories). There is the potential for certain additives to produce large absorbances between 200-400 nm, and this will need to be verified by running appropriate blank (no nitrite) samples. In this case, either test sample work-up or alternative methods of analysis such as LC- or GC-mass spectrometry can be used.

Secondary (and possibly tertiary) amines and amides will react to form nitrosamines/nitrosamides and produce absorbances in the UV region of interest (Chow, 1979). Fused-ring aromatic amines may produce large absorbances due to larger extinction coefficients, but it is unlikely these will be encountered as either solvents or additives.

The purpose of the UV irradiation/reaction chamber test is to establish the photolytic susceptibility of any nitrosamine/nitrosamide which might form. Each nitrosamine exhibits different resilience towards light in the UV-visible spectrum. More complex UV light degradation tests can be undertaken upon request from the vendor. For health and safety, it is recommend that an interlock switch is built into the reaction chamber

door that cuts power to the UV light source if the box is opened during operation. This will protect the operator from intense UV-light exposure.

5.6 Key capabilities and requirements

- a suitable wet chemistry lab with fumehood
- UV reaction chamber as described in the text
- UV-VIS spectrophotometer and appropriate cuvettes for absorbance measurement in the region 200-400 nm
- amber glassware for handling the reaction mixture.

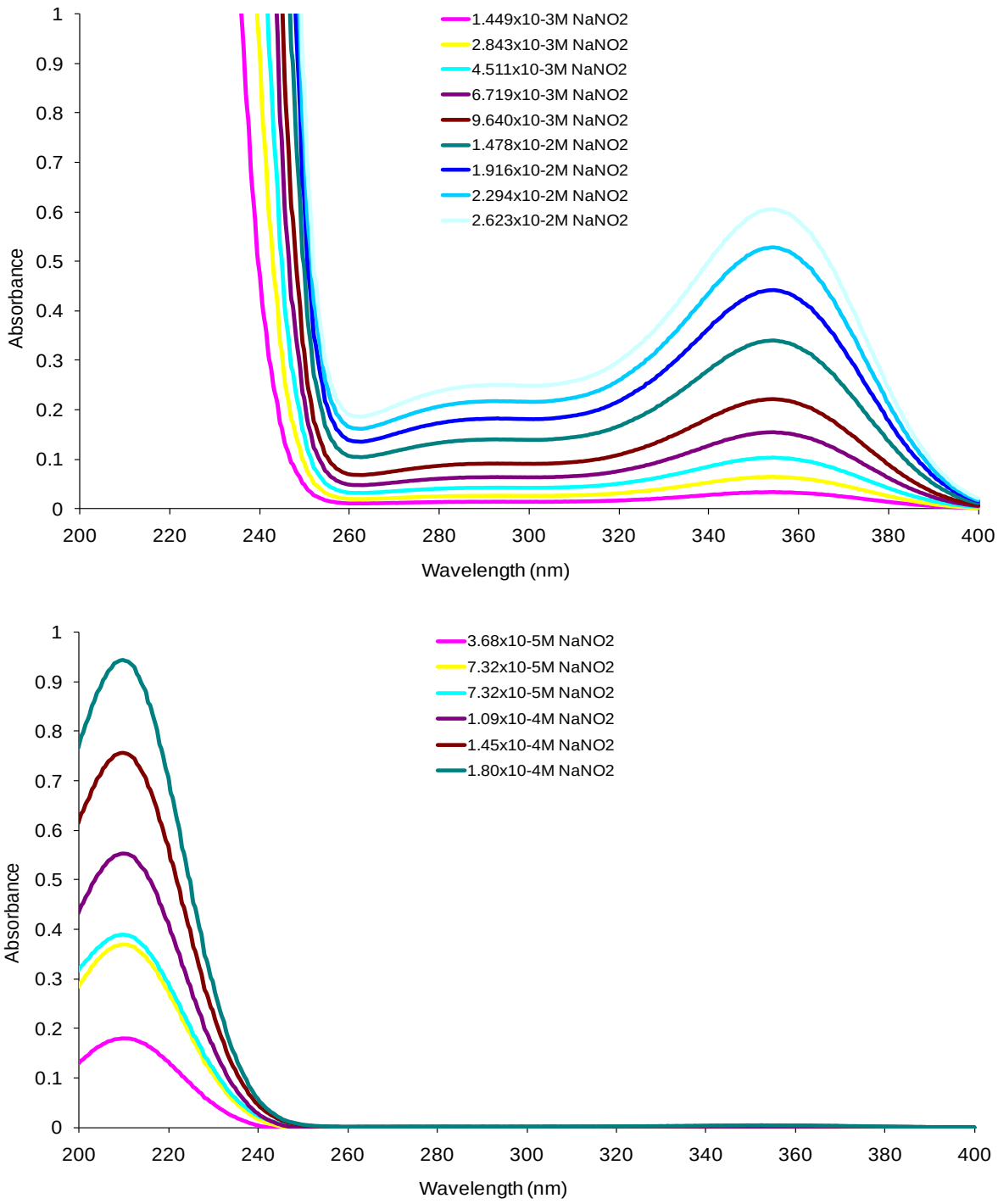

Figure 2. UV-visible absorbance spectra of nitrite (NO_2^-) ion.

6. PROTOCOL DETAILS: STEP TWO

6.1 General

Step two of the Protocol requires more sophisticated analytical instrumentation, as well as specialised purpose-built equipment to generate deleterious degradation and reaction by-products. The data analysis for this test step requires a well developed understanding of chemical kinetics. The operation of the analytical instrumentation also requires well-developed skills. Two tests are conducted in parallel: the first involves charging pressure vessels with up to 20 ml of aqueous solvent and a high-pressure (up to 2 MPa) headspace of CO_2 and/or CO_2/O_2. The pressure vessels are placed in an oven at a temperature in slight excess of the stripping temperature (to be agreed upon by the solvent vendor) for a period of up to 3 weeks. Liquid and gas test samples are taken for analysis. This test is described in Section 8.3.

In an experiment that is being run parallel to the pressure vessel degradation, a 200 ml volume of solvent in a round-bottom flask is sparged with a synthetic flue gas whose composition is representative of the power station flue gas (in terms of NO_x, SO_x, O_2, N_2 and CO_2). The laboratory sample is maintained at the vendor's recommended CO_2 capture temperature. Test samples are taken regularly and monitored for deleterious molecules such as nitrosamines and nitramines, as well as organic acids/aldehydes. This test is described in Section 8.5.

6.2 Purpose

To generate deleterious solvent degradation and capture by-product molecules in a short time frame (e.g. few weeks) using accelerated solvent degradation techniques in a safe/controlled environment.

The classes of compounds of degradation products determined in this step are summarised in Table 3 and listed in greater detail in the report on Project B Task 1, Table 4.

Table 3. Compounds analysed in Step 2.

Step	Degradation Products Tested For
2 part 1	Aldehydes, organic acids, volatile amines, amides
2 part 2	Nitrosamines, Nitramines

6.3 Experimental procedure (part 1)

A volume of aqueous solvent (~ 20 ml) is placed into each of two 316-stainless steel pressure vessels (see Figure 3). The head-space of the vessel is charged with

equimolar amounts of either CO_2 or O_2 or a mixture theoreof, to 2 MPa. The vessel is then heated to a temperature approximately 20 °C in excess of the recommended stripping temperature for 2-3 weeks (agreed by the vendor).

Higher temperatures may be required to effect degradation within a reasonable time-frame, and this will depend on the thermodynamic characteristics of the solvent.

At the end of the heating period, the laboratory samples are removed from the oven, cooled to room temperature, and a gas bleed performed under controlled conditions (see Section 4). A gas test sample is retained or captured using a gas bag (Teflon) and passed through a 2,4-DNPH sampling cartridge to trap any volatile aldehydes formed during degradation (analysis is with HPLC-ultraviolet fluorescence according to Lowe *et al*, 1981). An acid-impregnated cartridge can also be used at this point for capturing volatile amines. Preferably, a sampling train consisting of an impinger and several gas cartridges should be employed.

Figure 3. 316-stainless steel pressure vessels used in accelerated degradation studies.

The laboratory liquid samples are then divided into three (3) test samples, which are further sub-divided into test portions for replicate analysis and statistics. An example of the analysis to be performed for one portion is given below. This sequence is repeated for each of the pressure vessel samples.

Portion 1 is subjected to (i) ion chromatography (IC, in negative mode) for the analysis of organic acids. Portion (2) is subjected to IC in positive mode for the analysis of the primary amine and amine degradation products. For product identification, relevant standards need to be procured, and/or IC-MS employed for identification. This can be achieved by direct analysis with an in-line MS equipped with an API source operated in positive-ion mode. Alternately, the IC eluent fractions can be collected, and suitable derivatisations performed followed by GC or GC-MS analysis (eg. See Lepaumier *et al*, 2009). Any GC analysis requires follow-up sample preparation steps (extraction to a non-polar organic solvent and derivatisation), so IC followed by API-MS is possibly a more attractive option.

6.4 Discussion (part 1)

High pressure experiments should be performed in triplicate (total of 6 autoclave vessels) to remove bias in instances where the vessels were positioned in oven “hot spots”. K-type thermocouples should be fitted to the vessels to ensure the sample heating is uniform, and any oven temperatures are representative of the temperatures experienced at the centre of the pressure vessel. The purpose of the thermal degradation experiment is not only to identify products which may be deleterious in the first instance i.e. directly generated by degradation processes, but to also identify amides or other secondary amines which may react with the NO_x flue gas component to form nitrosamines or nitrosamides (in the liquor itself or in the atmosphere).

The autoclave technique of accelerated alkanolamine degradation is used in several laboratories around the world to enhance amine solvent degradation, and while it is not standardised between laboratories, it is widely accepted as a measure of amine degradability (Freeman and Rochelle, 2010; LePaumier *et al*, 2009).

Amides and other secondary amines which are identified as a result of the follow-up analyses are further investigated using the procedure described in step one (1) if they are available commercially. If the amides and sec-amines are not available for purchase or are not easily synthesised, the degradation samples can then be pooled and treated following step one of the Protocol (and analysed for nitrosamines/nitrosamides). The analysis for nitrosamines can also be performed with more sophisticated LC-MS analyses for more sensitive quantification.

Any organic acids identified in the degraded liquor (using IC) can react with amines to form amides, which can subsequently react to form nitrosamides. The organic acids detected serve as the basis for an analysis of amide-forming potential. The amides identified should be considered for their propensity to react with NO_x. The procedures described in Section 7.4 should be followed. In general, amides are not volatile, and amides with saturated aliphatic groups are usually non-toxic (Schultz *et al*, 2006). Nitrosamides themselves are extremely light sensitive (Chow, 1979), and while light sensitivity is an intrinsic molecular property, no predictions can be made without recourse to computational chemistry or experiments. For this reason, it should be assumed that any nitrosamides are just as toxic as nitrosamines or nitramines.

6.5 Experimental procedure (part 2)

A diagram of the gas absorption apparatus is presented in Figure 4. A simulated flue gas stream (3 or 4 components) is prepared using calibrated mass-flow controllers (Bronkhorst, all 0-1 L/min except 0-2 L/min CO_2) according to typical flue gas compositions specified by the solvent vendor. For the apparatus housed at CSIRO, the total gas flow rate used in previous experiments has been 1.34 L/min. As a number of nitrosamines/nitrosamides are known to be light-sensitive, the reaction vessel and any sub-sampling glassware are either amber or wrapped in aluminium foil. Flow is entrained through a 200 g mass of aqueous capture solvent maintained at the capture temperature specified by the vendor. The reaction mixture is sampled at 3 hour intervals, or less frequently depending on the NO_x or SO_x content of the synthetic flue gas. The $N_2/NO/O_2/CO_2$ content exhausted at the top of the reactor is de-humidified

using a commercial chiller, before being passed through an Horiba gas analyser or GasMet. The experiment can be run for many days or weeks in order to generate nitroso or nitramine molecules if the synthetic flue gas needs to be representative of a post-de-NO_X stream (~ 1 ppm). The test samples can be analysed using IC to study the temporal evolution of NO_2^- and NO_3^- in the liquor, while test portions can be analysed for nitrosamines using LC-MS. Note that the use of LC-MS circumvents the need for potentially hazardous liquid-liquid extractions prior to analyte measurement, but depending on the nature of the nitrosamines formed (volatile versus non-volatile), GC-MS may be preferred.

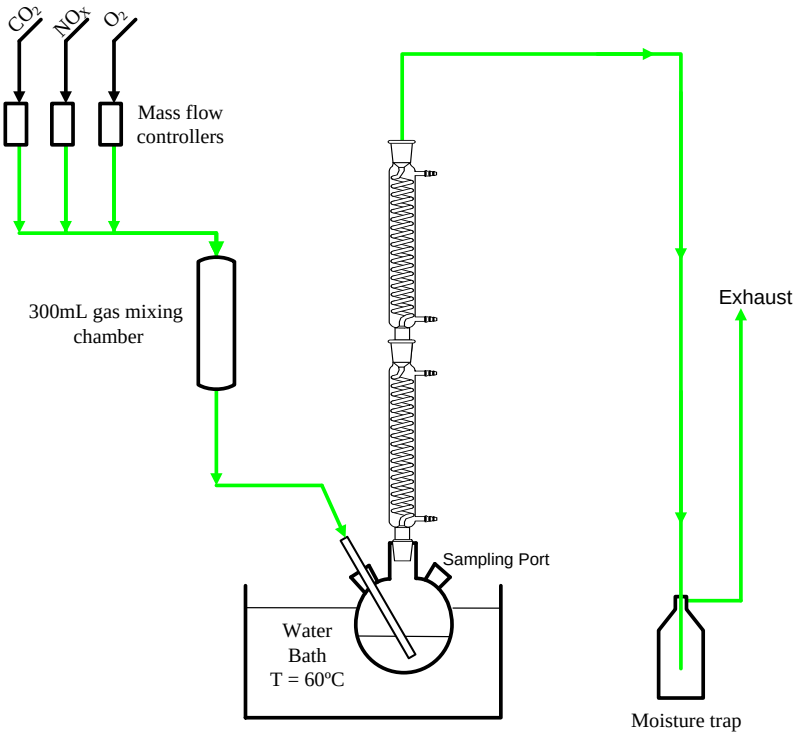

Figure 4. Schematic of the gas chemisorption apparatus.

6.6 Discussion (part2)

The purpose of this experiment is to determine the propensity of the vendor's solvent to form nitrosamines/nitrosamides (NA's/NAD's and possibly nitramines) under typical CO_2-capture conditions *in the condensed phase*. The study will reveal over the course of days/weeks (replicating low NO_x conditions) whether the solvent can accumulate N-centred deleterious molecules such as nitrosamines/nitrosamides/nitramines. Kinetic rate data can be obtained if a specialist oversees the work and interprets the results. The most demanding analysis is required if the rate of nitrosamine accumulations is low, and either LC-SIR-MS with < 5 ppm mass accuracy or LC-MRM-MS is recommended in this instance.

6.7 Key capabilities and requirements

- a suitable wet chemistry lab
- suitably rated inert (316 st.st. Teflon-lined) pressure vessels
- oven or fluidised sand bed capable of heating pressure vessels to ~ 250 °C
- means of capturing head-space gas ie. a gas bag or lecture bottle, and appropriate valves and st. st. tubing
- a chromatography capability with IC, LC- and/or GC/MS
- suitable glassware for sparging amine solutions at low pressure
- mass flow controllers for adjusting the composition of the synthetic flue gas
- IR gas analyser
- Water bath (20-90 °C)

7. PROTOCOL DETAILS: STEP THREE

7.1 General

This step involves a further incremental increase in the complexity of:

- the testing apparatus
- sample collection
- sample analysis.

This also represents the final experimental analysis (with the possible exception of smog chamber studies) prior to pilot-scale trials. The lab-based approach maximises understanding of the process chemistry under controlled -but realistic- CO_2-capture conditions. The laboratory represents a safe, controlled environment.

The apparatus for this step is designed for repeated sorbent cycling for long periods (months) at the absorption and regeneration temperatures suggested by the vendor. The apparatus is capable of producing/controlling a more complex synthetic flue gas mixture (up to 6 or 7 components). Similar to a pilot plant, the lab scale apparatus is 'switch on/switch off'. Solid fly-ash or other minerals can be added to the apparatus to elucidate any catalytic-degradation effects these materials might confer – as needed. Any solids added would be representative of fossil fuel combustion residues that the solvent would encounter during field operation. The cycling period shall run for several months (possibly until the solvent requires base-charging or when the level of heat-stable salts impairs capture performance). Solvent lifetimes can be determined during the testing period with feedback from the analytical test results. The most sensitive and reliable analytical testing methods should be employed at this step of the Protocol; based on CSIRO experience, LC-MS/MS and ion chromatography should be used to analyse the capture solvent, while GC-MS should be used to analyse any pollutants trapped using volatiles gas-sampling cartridges. A flow process diagram of a typical laboratory-scale solvent-cycling apparatus is presented in Figure 5. The diagram is based on the design of the apparatus housed at the Energy Centre, CSIRO, Newcastle, Australia.

7.2 Purpose

To monitor solvent degradation for much longer periods (e.g. months) in a controlled environment under capture conditions specified by the vendor. This will allow identification of degradation intermediates which may not have been detected in step two (2). Lab-scale emissions can be measured and an estimate of losses obtained.

The classes of compounds of degradation products determined in this step are summarised in Table 3 and listed in greater detail in Project B Task 1 Table 4.

Table 3. Compounds analysed in Step 3.

Step	Degradation Products Tested For
3	Aldehydes, organic acids, volatile amines, amides, nitrosamines, nitramines

7.3 Specific design features

With reference to Figure 5:

- 2 round-bottomed flasks with a capacity for a solvent charge of 3-5 L
- 2 liquid pumps, variable pumping speed up to 3 L/min, 2 m head
- 2 condensers
- mass flow controllers (> 5), for a composite synthetic flue gas flow rate up to 10 L/min
- means of rapidly heating the laboratory sample to temperatures up to 170 °C (CSIRO employs a commercial fryer and st. st. tube heat exchanger for this purpose)
- glass columns designed for packing with raschig rings, and two appropriate shower heads
- chiller units for temperature control of the lean- and loaded-laboratory sample
- an air pump, appropriate teflon tubing and divert valves for drawing exhaust gases through a bank of gas cartridges
- a tube heat exchanger for cooling the lean liquor from the regenerator
- a CO_2 flow meter for mass balance of the regeneration exhaust gas
- miscellaneous Teflon tubing, tygon tubing, K-type thermocouples
- glassware for impingers
- gas pump for drawing exhaust gas through gas-sampling cartridges and a mass flow meter
- material for lagging

Sampling points in Figure 5 are indicated for the solvent (blue circles) and the exhaust gas streams (red circles). A liquid impinger (either 0.1 M HCl or 0.1 M KOH with an added radical scavenger such as ascorbic acid or sulfanilic acid (Baptist and Brown 1980) is recommended for the capture of volatile polar pollutants. The impinger should be placed up-stream of any gas-sampling cartridges.

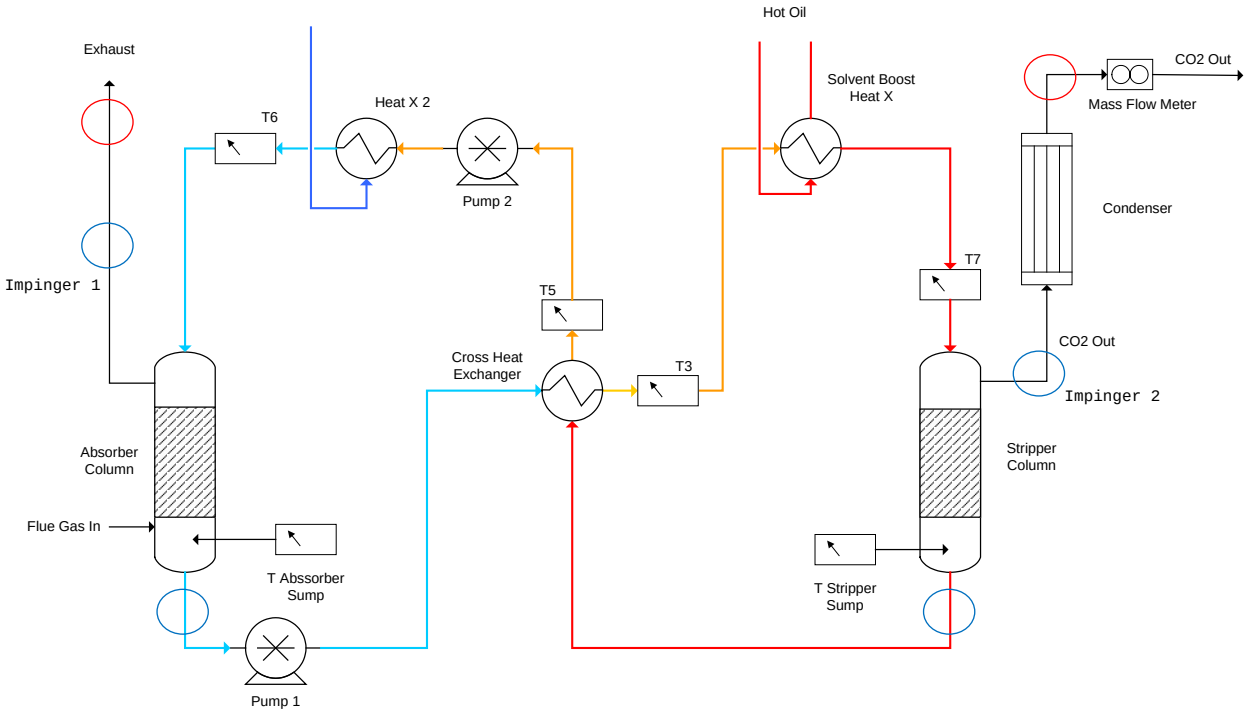

Figure 5. Schematic of the solvent cycling apparatus. Blue circles = solvent sampling points; red circles = gas sampling points

In order to preserve any nitrosamines that might be formed, amber sampling glassware and aluminium foil should be used to exclude stray light. Silylation of glassware can be used to maximise detection sensitivity.

8. PROTOCOL DETAILS: STEP FOUR

8.1 General

The fourth Step in the amine-based CO_2 capture technology Protocol includes the examination and provision of evidence that the emissions from the plant to the environment will be within acceptable air quality standards. Harmful compounds identified in Project B Task 1 that are expected to be released to the atmosphere, need to be assessed for their potential environmental impact.

This Step represents the synthesis of all the information obtained on the target PCC solvent from Steps 1 to 3 in order to assess any potential environmental and health effects.

8.2 Purpose

To carry out a rigorous assessment of the potential environmental impact of any harmful compounds (and their atmospheric reaction products) as identified in Steps 1 to 3.

8.3 Procedure

For all pollutants one of the key inputs required for the assessment of their air quality impact is their *emission rate*. While this can sometimes be provided by direct measurement, in the case of PCC plants it is likely that in the first instance the emission rate data will be derived from process (chemistry) modelling. However, in terms of subsequent environmental impact each potentially harmful species must be considered both in terms of its toxicity and the rate at which it is emitted and then dispersed in the atmosphere. In this context, air quality assessment is a well developed branch of science and engineering with many standard models in use across the world (http://www.epa.gov./scram001/) Nevertheless the processes involved in determining the air quality impact for a given pollutant can be quite complex and require expert knowledge.

In considering pollutants it is critical to establish the atmospheric fate of the compounds. While some compounds (eg SO_2 and NO_x) have been studied worldwide for many decades most of the emissions anticipated to arise from PCC processes have not. Consequently it is important to consider whether the pollutants identified in Steps 1 to 3 are *reactive* or *unreactive*, and if *reactive*, whether their chemistry is *known* or *unknown*. The pathway followed below for each compound will then depend on these factors.

The steps to be followed are:

1. Results obtained from Step 1 to Step 3 will be used along with chemical process modelling (eg Aspen Plus) to establish emission rates for all known and anticipated emitted compounds and whether in the gas or liquid phase.

2. These results will be used along with toxicity databases to identify the toxicity associated with all identified species. Relevant information for each compound will be obtained from readily available sources (eg EPAs, NIOSH, WHO and regulatory agencies).

3. Based on (1) and (2) above compounds that represent a risk to human health and the environment, will be classified as *reactive* or *unreactive*.

4. For *unreactive* species an appropriate plume model suitable for the selected domain will be used to model the dispersion and ground level concentrations of these pollutants. Results will be compared to local government air quality regulations.

5. In some cases air quality regulations may not cover the chemical species being modelled and in these cases general toxicity and health related information will need to be used (where available) to make informed judgments as to the significance of these compounds

6. *Reactive* species will be classified as possessing *known* or *unknown* atmospheric degradation chemical pathways.

    a) For *known* chemical pathways, the chemical reaction mechanism describing the degradation process will be used in an airshed model to calculate the spatial and temporal profiles of reactive pollutant concentrations. The environmental impact assessment can be determined using these concentration data.

    b) For species with *unknown* degradation pathways, quantum chemical modelling is highly recommended. A great advantage of quantum chemical modelling is that conditions which are difficult to examine experimentally can be studied with ease e.q. OH abstracting hydrogens from MDEA would be relatively easy to study, and would produce meaningful branching ratios, whereas the low volatility of MDEA renders a smog chamber study very difficult at best. There are few limits to the compounds that can be studied using quantum chemistry, although the time required to model degradation scenarios completely and accurately will increase dramatically with increasing molecular size and complexity.

    c) For species with *unknown* degradation pathways, smog chamber experiments may be required to obtain data to develop the appropriate chemical mechanisms to describe their behaviour. To facilitate the design of experiments, it is recommended that the

composition of real world PCC emissions be determined as soon as possible and that a “common” composition matrix be developed that is representative of the range of concentrations expected from a PCC plant. Please also refer to the recent CSIRO study EP101723 (Angove *et al*., 2010) on MEA for a greater understanding of the matrix concept.The design of airshed experiments is dependent upon knowledge of the composition of emissions. However, this does not preclude (i) performance of chamber experiments to investigate mechanisms or (ii) use of the chamber to generate nitroso- compounds safely in the gas phase to support analytical method development. Two types of chemical mechanism can be developed. The first one is a simplified chemical scheme that can be used as a screening technique and the second one is to produce a lumped scheme of the chemical degradation processes. The latter will be used for more comprehensive air quality assessment.

7. Information on the deposition on soil and water bodies will also be available from the plume and air quality modelling.

8. Ecotoxicology due to any uncontrolled releases of the solvent and process liquor should also be assessed using the appropriate ecotoxicology tests.

It is important to highlight that fugitives may be another source of emissions from a PCC plant. These emission rates will be estimated using well established methods (http://www.arb.ca.gov/fugitive/fugitive.htm). Once the strength of these emissions has been determined the procedure outlined above, will also be applied to these.

8.4 Key capabilities and requirements

- Smog chamber facilities as described in appendix D
- toxicity screening capabilities
- Aspen™ or other suitable mass-balance process and equipment modelling software
- ability to develop chemical reaction schemes describing the atmospheric chemistry of pollutants and to predict air quality using sophisticated Lagrangian and Eulerian grid based models.
- computational chemistry with access to supercomputing facilities

A comment on the merits/drawbacks of quantum chemistry is warranted at this point. As mentioned above, there are few limits to the compounds that can be studied using quantum chemistry, although the time required to model degradation scenarios completely and accurately will increase dramatically with increasing molecular size and complexity.

The accuracy of the results predicted by quantum chemistry is largely dependent on the level of theory used and the size of the basis set used to describe the atoms in the molecules. An accuracy of $|\text{theory} - \text{expt}| < 2$ kcal/mol should be the goal of any gas-phase quantum study. Higher levels of theory i.e. at least CCSD(T) with larger basis sets (augmented triple zeta, preferably correlation consistent) are recommended. The decision regarding the level of theory and resources needed for any study should be made by quantum experts after consultation with the client.

Gas-phase results can be very accurate (within 2 kcal for heats of formation, within 2.5 kcal for activation energies, see Zhao and Truhlar, 2008), however the accuracy of aqueous reaction energies and equilibrium constants determined using continuum reaction field methods is highly variable, as this area is relatively new or immature. Rapid progress is however being made. SMx solvent models are promising, however the uncertainties in the free energies of solvation ($\Delta G_{solvation}(A)$) predicted by these methods is still much greater than the uncertainty for gas phase free energy values, hence solution or aqueous phase energetics are not as reliable, since $\Delta G_{aq}(A) = \Delta G_{gas}(A) + \Delta G_{solvation}(A)$, and any errors are additive (the gas phase free energy of formation is needed to determine the aqueous free energy of formation, as described by the equation given above).

9. PROTOCOL DETAILS: STEP FIVE

9.1 General

Step five (5) is the testing body-client/vendor reporting stage. A scorecard incorporating the results from steps one (1, Section 5) through four (4, Section 8) is presented to the client. The results are reported against a reference which shall be a generic solvent such as 30 % wt aqueous MEA. A period of 3-6 months from vendor sample submission until report delivery is envisaged. After consultation with the testing body, the vendor can choose to proceed with pilot scale testing or reformulate the solvent to comply with local regulations\emissions legislation. An example of vendor report is described in Appendix C.

9.2 Purpose

The purpose of this step is to report the results of the testing back to the vendor with the option of proceeding towards the pilot plant testing.

9.3 Key capabilities and requirements

Details of a representative CSIRO pilot plant deployed at a regional power station is described in appendix E.

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11. ACKNOWLEDGEMENTS

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APPENDIX A – COMMENTS ON NITROSAMINE/NITRAMINE LITERATURE AND CHEMISTRY

Due to the potentially harmful nature of all chemicals with N-NO and N-NO_2 functional groups, the literature covering the thermodynamic properties of those pollutants with this functionality is scarce due to the risks of conducting such research. Most open literature focuses on nitrosamine presence and detection in foodstuffs (Sen *et al*, 1990; ; Havery *et al*, 1982; Rappard *et al*, 1976; Scanlan *et al*, 1980; Ventanas andRuiz, 2006a; Ventanas and Ruiz, 2006b), cosmetics (Volmer *et al*, 1996a; Volmer *et al*, 1996b), cigarette smoke (Jansson *et al*, 2003; Jacob III *et al*, 2008; Shah *et al*, 2009), polluted air (Rounbehler, *et al*, 1980a; Krost *et al*, 1982; Tuazon *et al*,1984; Marano *et al*, 1982; Rounbehler *et al*, 1980b) and drinking waters, as a by-product of disinfection (Cheng *et al*, 2006; Mhlongo *et al*, 2009; Schreiber and Mitch, 2006). Nitramine data in the open literature is limited to their explosive properties (Leszczynski and co-workers, 2008; Ge *et al*, 2007; Bernstein and co-workers, 2007), with the exceptions of a few papers dealing with their detection in complex matrices (Tachon *et al*, 2007; Crescenzi *et al*, 2007; Groom *et al*, 2001; Gaurav *et al*, 2007). The body of work represents a useful guide for sampling, and useful methods of detection can be identified. For these compounds, thermodynamic data which would be useful for process modelling is not available (see discussion, Project B Task 1). Note that small, secondary alkylamines are too volatile to be deployed as CO_2 capture solvents at the commercial scale, and there is limited information that suggests that these molecules are either solvent- or atmospheric-chemical degradation products derived from common CO_2-capture amines. The published literature concerning nitrosamine derivatives of small, volatile amines focuses on N-nitrosodimethylamine and other nitrosoalkylamines, specifically their detection. There is some information available for the N-nitroso derivative of diethanolamine (Tunick *et al*, 1982; Edwards *et al*, 1979; Flower et al, 2006; Schothorst and Somers, 2005) due to the ubiquity of this alkanolamine in cosmetics.

Note: In Appendix A, information is presented which was obtained at CSIRO prior to undertaking any work as part of the CCM programme. *CSIRO has submitted, or intends to submit, this data to journals for publication. This information:*

- *remains confidential until such times that it appears in the open literature, and*
- *shall not be disclosed without CSIRO permission.*

The experimental procedure for the detection of N-nitrosopiperazine within PCC-like solvents is detailed in the attached manuscript that has been submitted to the journal *Rapid Communications in Mass Spectrometry*, by Jackson and Attalla (2010). A paper presenting aspects of this material has also been presented at the Clean Coal and Energy Systems Conference in Clearwater, Florida, July 2010. The method used throughout also forms the basis of Step Two (2) part two (2, Section 8.5) of the Protocol. The results discussed for DEA, MDEA, AMP and 2-piperidinemethanol have recently been submitted to the open literature *in a preliminary form*.

Following the procedure outlined in Section 8.5 of the Protocol, and in the absence of solvent regeneration/CO_2 stripping, CSIRO have generated and identified the N-nitroso derivatives of common secondary capture solvents such as diethanolamine, piperazine and 2-piperidinemethanol (a “hindered” secondary amine). Similar experiments have

been undertaken for methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP) and 2-aminoethanol (MEA). The investigation of hindered primary amines and tertiary amines under CO_2-capture conditions is ongoing, but for these solvents there was no spectroscopic evidence of N-nitroso derivatives being formed in significant quantities. This finding is consistent with published literature (Challis and Kyrtopoulos, 1979 and references therein). This is in contrast to the secondary amines listed above. N-nitrosopiperazine was selected for further investigation as part of this work. Both N-nitrosopiperazine and 1,4-dinitrosopiperazine were identified in the reaction mixture, and exposure to regeneration temperatures (160 °C) for a short duration (up to 20 mins) did not result in significant degradation (Jackson and Attalla, 2010). Secondary amines form long-lived nitrosamines in solution (Challis and Kyrtopoulos, 1979 and references therein), however their stability varies, and is dependent on intrinsic molecular properties e.g. photolytic susceptibility (Fiz *et al*, 1993; Grover *et al*, 1987). There is a publication which indicates heat and $NO_2^{\square}$ may induce cyclisation in primary diamines; in turn this generates secondary amines and nitrosamines (Warthesen *et al*, 1975). A compendium of CSIRO publications covering this subject matter is attached to this document.

The chemical mechanisms of nitrosamine formation are ill-defined. A general mechanism has been proposed for solutions at low pH (Wang *et al*, 2002), which is presented below for reference purposes only:

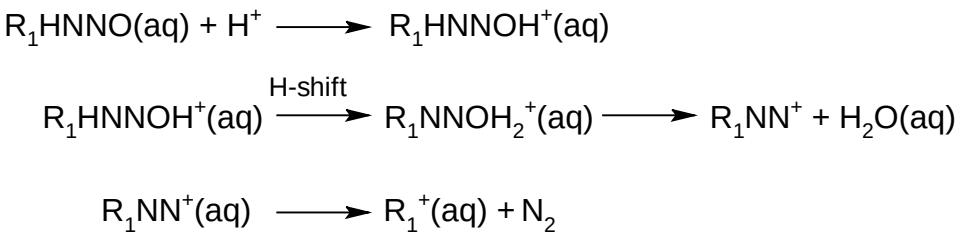
$$NO_2(g) \longrightarrow NO_2(aq) \xrightarrow{H_2O} HONO(aq)$$

$$HONO(aq) \xrightarrow{H^+} H_2ONO^+(aq) \longrightarrow H_2O + NO^+(aq)$$

$$NO^+(aq) + R_1R_2NH(aq) \longrightarrow R_1R_2NNO(aq) + H^+$$

Scheme 1. Mechanism of nitrosamine formation at low pH from secondary amines.

There are a number of reasons cited for the *instability* of nitrosamines derived from primary amines; Scheme 2 is a proposed mechanism for the *degradation* of primary nitrosamines at low pH (Wang *et al*, 2002). The reaction scheme follows from Scheme 1 above, however one of R_1 or R_2 in the case of a primary amine in Scheme 1 is a hydrogen atom:

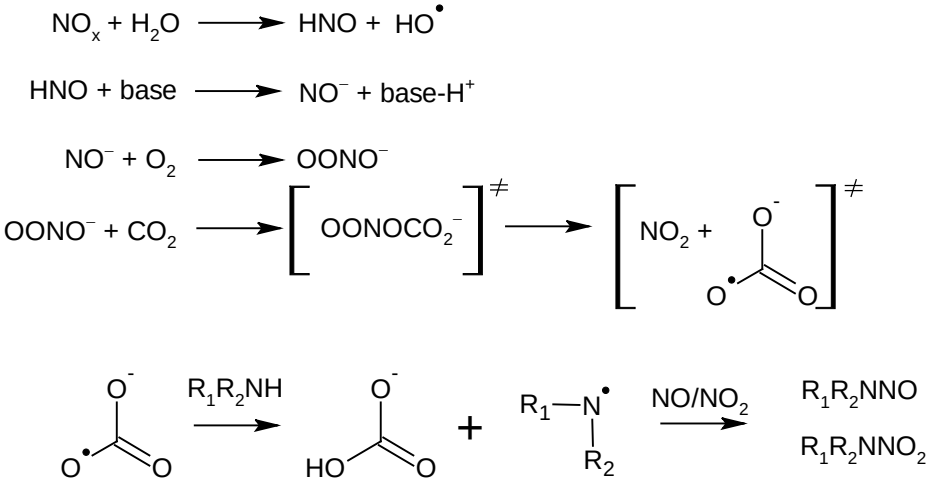


Scheme 2. Mechanism of primary amine nitrosamine decomposition at low pH.

A number of nitrogen oxides have the potential to form nitrosamines (e.g. HNO, N_2O_3, N_2O_4, NO^+, ONOO (Challis and Kyrtopolous, 1979; Hughes 2008; Hughes 1999). At neutral (physiological) pH, Goldstein and Czapski (1996) derived a rate law for the nitrosation of thiols and morpholine in oxygenated solution, which was found to be independent of the substrate being nitrosated:

$$-d[NO]/dt = 4k\,[NO]^2[O2] \qquad (1)$$

This is essentially identical to the rate law for oxidation of NO to NO_2. Reaction of O_2 with $NO^{\square}$ (generated by dissociation of nitroxyl acid, HNO) produces peroxynitrite ion, $ONOO^{\square}$. This ion reacts rapidly with CO_2 to form $ONOOCO_2^{\square}$ (Hughes, 2008). Disproportionation of the nitrosoperoxycarbonate anion yields $CO_3\bullet^{\square}$ + $\bullet NO_2$; the former species can react to abstract a hydrogen atom from an amine substrate to form a radical aminyl species and $HCO_3^{\square}$. Subsequent reaction with either NO or NO_2 (which are both radicals) will yield a nitrosamine or nitramine. During the disproportionation process, NO_2 could oxidise the aminyl substrate to produce an N-oxide derivative and NO. CSIRO have detected an N-oxide derivative in 15 % wt solutions of piperazine sparged with a synthetic flue gas (Jackson and Attalla, 2010). Based on this information, the most probable mechanism of nitrosamine/nitramine formation under PCC capture conditions is presented in Scheme 3.



Scheme 3. Proposed mechanism of nitrosamine formation at high pH.

APPENDIX B – CHEMILUMINESCENCE ANALYSIS OF PCC SOLVENTS

Introduction: This procedure is an alternative to the UV-VIS analysis described in step one (1, Section 7.3) of the Protocol. This procedure follows step one (1) up to and including the DCM drying step with anhydrous sodium sulphate.

Experimental: WARNING! ALL NITROSAMINES ARE POTENTIAL CARCINOGENS AND SHOULD BE HANDLED WITH CARE TO AVOID EXPOSURE. Add the dry DCM containing the analyte to a stoppered gas-tight bubbler assembly with two (2) gas necks and a septum for adding liquids using a hypodermic syringe. One neck possesses a dispersion frit for sparging the reaction mixture using a carrier gas such as argon or nitrogen (argon is preferable). After adding the reaction mixture, a suitable volume of make-up DCM is added to ensure the frit is completely immersed in the reaction mixture (make up the volume to say, 60 ml with DCM; the volume must remain constant for all quantification analyses). The other neck is connected to a chemiluminescent NO analyser. A steady carrier gas flow is set (this value will depend on the detector performance); a flow of ~ 180 ml/min is suggested (but adjustment above or below such a value might be necessary depending on the sharpness of the detector response and whether the detector possesses a gas pump). The remainder of the procedure follows the method of Drescher (Drescher and Frank, 1980). 2 ml of acetic anhydride is added through the septum to scavenge any water, then 0.2 ml of 48 % HBr in glacial acetic acid (1.7 ml HBr in 25 ml glacial acetic acid) is added as denitrosation catalyst. The chemiluminescence analysis begins upon addition of the denitrosation catalyst. Consult the relevant chemiluminescence detector specifications sheet for further instructions on how to proceed with the analysis.

Frank and Drescher have reported:

- linear detector response over the range 5×10^{-9} M to 5×10^{-6} M
- a standard deviation for the diethylnitrosamine detection limit (7×10^{-9} M) of 3.5 % was measured

APPENDIX C – EXAMPLE VENDOR QUESTIONNAIRE/TEST REPORT SHEET

VENDOR QUESTIONNAIRE			
Name:	**Date:**		
Solvent identifier:	**Patented?**	Yes	No
Country of PCC plant operation:			
Name of government authority or agency issuing emissions permits?			
Closest city/township to PCC plant operation:			
MSDS sheets attached?		Yes	No
Solvent class? E.g. amine blend, aqueous secondary amine etc.			
Any other information provided by vendor regarding solvent class?			
Does the solvent contain:			
Corrosion inhibitors?		Yes	No

Anti-fouling additives?	Yes	No
Any other additives?	Yes	No
MSDS sheets provided?	Yes	No
Provide any vendor information here:		

Vendor recommended absorption temperature:	
Vendor recommended regeneration temperature:	
Optimal solvent rich loading:	
Optimal solvent lean loading:	
Does solvent form a carbamate?	

Circle flue gas type:	Brown coal		Black coal		Natural gas			
Approximate flue gas composition (%):	N_2		CO_2		O_2		H_2O	
Flue gas contact temperature:								

NOx level (ppm)	
SOx level (ppm)	
Fly-ash mineral composition:	

TEST RESULTS SHEET			
Testing body:		**Date:**	
Person to whom representations regarding test results should be made:			
Solvent identifier:			
Test 1: **UV nitrosamine absorbance maxima:**			
Solvent forms nitrosamines ?		Yes	No
Nitrosamines degrade when exposed to UV light?		Yes	No
Nitrosamines degrade faster when exposed to:	UVA	UVB	UVC
Feedback provided to vendor?		Yes	No
Proceed to Test 2?		Yes	No
Comments:			
Test 2 results: **Is the solvent severely degraded?** **Viscosity of degraded product:** **CO_2** **CO_2/O_2** **Carbamate (CO_2) degradation products:**	**Percentages:**		

Secondary amines identified in carbamate degradation products? **Specify:**			
Oxidative degradation products: **(non acids)**	**Percentages:**		
Organic acids:	**Percentages:**		
Volatiles:	**Percentages:**		
Rate of nitrosamine formation at vendor's specified NO_x and O_2 flue gas composition:			
Vendor feedback supplied?		Yes	No
Date of feedback:		**Date:**	

Proceed to Test Step 3?	Yes	No
Vendor requests fly-ash added?	Yes	No
Date Test Step 3 commences:	**Date:**	
Dates liquor is sampled:	**Dates:**	
Dates volatiles are sampled using cartridges (include cartridge type): **Dates volatiles are sampled using impinger:** **Total run time:**	**Dates:**	
Percent CO_2 captured on first day:		

Percent CO_2 captured on last day:	
% deterioration in solvent performance:	
ATTACH TEST ANALYSIS RESULTS HERE	
Comments:	
Major degradation products: **Major degradation products with potential to form nitrosamines/nitramines:**	
Unidentified volatiles detected?	
Rates of degradation:	

Reference rates of 30 % wt MEA degradation:		
Concluding remarks and recommendations: **Degrades faster/slower than 30 % wt MEA?**		
Degrades faster/slower than 30 % wt MEA?	Yes	No
Feedback provided to vendor?	Yes	No
Date provided:		
Proceed to Step 4?	Yes	No
List local regulations governing emission of pollutants:		
Attach Process and equipment modelling results here:		
Attach toxicity testing results here:		
Atmospheric lifetimes of volatiles from literature:		

***Ab initio* computations recommended?**	Yes	No
Smog chamber modelling recommended?	Yes	No
Recommendations:		
Feedback provided to vendor?	Yes	No
Authorising Signature:		

APPENDIX D - CSIRO SMOG CHAMBER

Over the last 40 years CSIRO scientists have contributed to the understanding of photochemical smog formation using indoor and outdoor smog chambers and have developed photochemical smog models (such as GRS and IER reactive plume models) that are used for air quality assessments as well as the development of control strategies. In the 1990's, CSIRO developed a universal photochemical monitoring system, the AIRTRAK system (Johnson and Quigley, 1989), to provide rapid, on-line measurements of the reactivity of small air parcels over a wide urban region. The system can also provide information about the age of a given air parcel, which is needed for source-receptor apportionment. The use and update of the AIRTRAK system for the near, real time assessment of PCC plant emissions may be advantageous to PCC plant operations, especially, with respect to emission control. It should be noted that the application of the AIRTRAK technology to PCC will require further development..

Amines have a high reactivity towards the hydroxyl radical (OH), which is abundant in the atmosphere during daytime. The indoor smog chamber is a powerful option that can be used to elucidate the atmospheric reactions between amines and other components existing in the surrounding air. The use of an indoor smog chamber allows control of initial conditions which are representative of ambient conditions, such as light intensity and humidity. Recommendations concerning the use of the CSIRO smog chamber to support such theoretical studies are given in Project B Task 2 and summarised briefly here for ease of reference.

1. Provide the observational data needed to develop and validate chemical reaction mechanisms needed to carry out air quality assessment
2. Identify most abundant and major products of the atmospheric degradation of a selected chemical compounds
3. Provide the data needed to demonstrate the accuracy of the computational quantum chemistry predictions before being used.

The CSIRO smog chamber is unique in the Southern Hemisphere and is recognised internationally. It is fully equipped for photochemical smog measurements and for secondary organic aerosol studies, including aerosol sampling. Apart from precursor injection facilities the chamber allows real time continuous measurements of O_3, NO and NO_2 (measured as NO_Y-NO) and NO_Y. A 119 m long-path FTIR system can be used to measure other species such as CO, NO_2, HNO_3, HCHO and has already been used to measure amines such as MEA, diethylamine and nitrosodiethylamine. Major hydrocarbons are measured by canister grab samples and GC. A new generation GC/MS/MS has recently been acquired to enhance this technique. Major carbonyls are measured by DNPH cartridge/HPLC. During all experiments the secondary organic aerosol number distribution can be monitored by SMPS (scanning mobility particle sizer) results from which can be used to calculate aerosol mass.

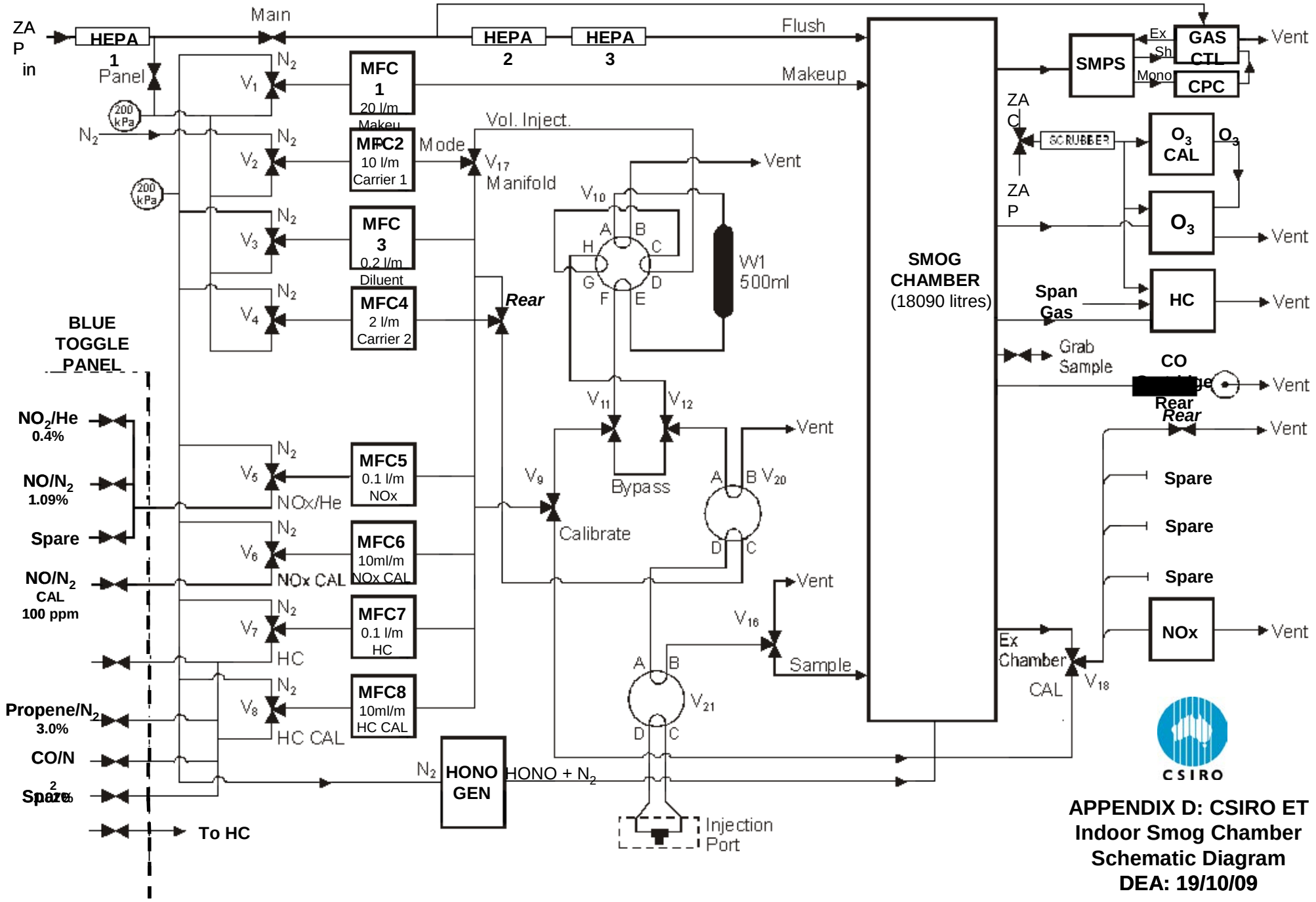
As well as play a significant role in the recommended theoretical studies, the CSIRO chamber can be us to develop and verify gas phase sampling and analytical methods. The chamber can be used in it its non-experimental UV mode or dark mode to present test atmospheres to sampling/analytical methods to determine uptake, collection stability, storage stability prior to analysis and recovery. This application is valid for both field and laboratory based collections. The chamber can also be used to explore control options for nitrosated compounds dependent upon UV photolysis techniques.

The formation of gas phase nitrosoamines and nitramines is problematic. The HONO vapour injection system utilised by CSIRO maybe adaptable for the preparation of trace levels of nitrosoamines and nitramines under safe conditions. However, it should be noted, this is an investigative task.

The CSIRO indoor smog chamber has already been used to explore the kinetics of the MEA/NOx system. This study relied on the development of a low loss MEA injection system. This technique maybe adaptable to PZ, but DEA and MDEA will require further development, such as injection by entrainment, to explore their gas phase chemistry.
A schematic of the Smog Chamber is presented in Figure 9.

The smog chamber in relation to generic solvents: according to the scope of work described for CCM Amine B Tasks 1-3, the targeted species for testing include 30 wt % MEA + heat stable salts (HSS's), PZ-promoted AMP, and MEA-promoted MDEA.

HSS's are not volatile but will *promote* secondary organic aerosol formation in the atmosphere if significant amounts are entrained in droplets. MEA itself is a candidate for smog chamber experiments, and has been studied at CSIRO. PZ is not volatile, however smog chamber experiments might be possible with a suitable volatilisation technique. AMP is a suitable candidate for smog chamber studies. MDEA is not volatile but is a suitable candidate for *ab initio* methods, as it will escape in droplets. All the alkanolamines have significant dipole moments and will promote aerosol formation. A ranking in terms of gas-phase reactivity is not possible at present as the experimental and theoretical databases are incomplete. In terms of nitrosation, and excluding degradation products from consideration, PZ-promoted AMP has the highest potential to form nitrosamines. To the best of our knowledge, all alkanolamines can degrade to form secondary amines or amides under certain thermal or oxidative conditions. Nitrosation potential will need to be studied on a case-by-case basis in this instance. Once a complete degradation dataset is available for a particular solvent, an assessment of nitrosating potential can be made, and the volatility of specific degradation products can be assessed for smog chamber experiments. Note that small amides such as formamide and acetamide are not volatile, so an amide assessment may only need to involve consideration of (i) nitrosating potential and (ii) promotion of aerosol formation.



APPENDIX D: CSIRO ET Indoor Smog Chamber Schematic Diagram DEA: 19/10/09

APPENDIX E - CSIRO PILOT PLANT CAPABILITY

E.1 GENERAL

The PCC plant described below demonstrates PCC at pilot scale on real flue gases from combustion sources. The pilot plant addresses the capture of CO_2 in installations which may or may not have the SO_x and NO_x capture technologies which are commonly deployed in Europe, the US, and Japan.

The PCC pilot plant is designed to operate with low temperature chemical solvents (below 130°C) but primarily with alkanolamine-based solvents. It may be adapted for other solvents.

The target application is performance testing of the post combustion capture of carbon dioxide from dilute flue gases. The process involves contacting the cooled flue gases with a spray, or surfaces wetted with the sorbent. This gas-liquid contacting allows the sorbent to capture CO_2 from the flue gases. The remaining gases are vented. The CO_2-rich sorbent solution is then heated to strip the CO_2, into a near pure gas stream. The CO_2-lean sorbent solution is then cooled and returned to the absorber column. The stripped CO_2 is compressed, dehydrated, liquefied, and pumped to pipeline pressure. A simplified schematic of the process is provided in Figure 6.

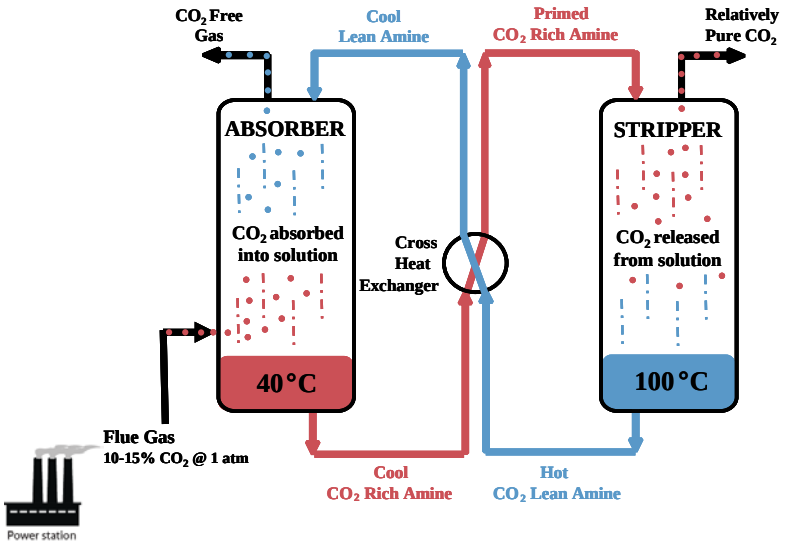


Figure 6. Flow diagram of the principle process governing the removal of CO_2 from flue gas by an aqueous amine solution.

E.2 PLANT CONCEPT DESIGN

The CSIRO PCC pilot plant is used to perform R&D into CO_2 capture from real flue gases, at a scale sufficient to fully characterize capture performance, solvent degradation and operating issues for a selection of solvents, operating strategies and process configurations. It is able to operate with reboiler temperatures up to 140°C and operating pressures up to 10 bar (design up to 15 bar). The pilot plant also offers the capability to:

- Continuously operate, up to 3 months at a time
- Retrieve experimental data relating to alternative process configurations and optimizations that have been suggested to reduce the energy and resource usage of CO_2 capture
- Determine the effect of high SOx and NOx levels in the flue gas on the operation/economics of an amine based CO_2 capture plant. SOx/NOx expected to affect solvent use/degradation
- Interrogate the following interrelationships:

    1. CO_2 capture energy consumption
    2. CO_2 capture efficiency
    3. Solvent CO_2 loading
    4. Solvent and flue gas flow rates
    5. Regeneration temperature and pressure
    6. Absorption temperature
    7. Solvent consumption and degradation rates
    8. Fouling and corrosion
    9. Effectiveness of the conditioning stage
    10. Reagent loss rate both to product CO_2 gas and to CO_2 lean flue gas
    11. System water consumption

The design of the pilot plant is flexible as possible to allow these assessment activities to be undertaken to ensure:

- Ease of access for maintenance
- Ease of access for performing modifications to plant for investigating other process configurations.
- Reconfiguring gas and liquid sample points to enable effects of process modifications to be determined.
- Changeable column design to enable rerouting of liquid flows and changing of packing heights to effect plant performance due to changes in operation strategies or solvents.
- Take off and inlet points for additional equipment to be added, changed and removed.
- Continuous operation during power station unit down time by providing multiple inputs from 2 different power station units.

E.3 DATA COLLECTION

The process has a wide range of operating parameters that can be monitored and/or controlled to ensure safe, efficient and reproducible operation of the plant as well as providing useful information for further understanding the process and its scalability:

- Flue gas flow
- pH of the bottoms liquid in the flue gas direct contact cooler
- Desulphurisation agent consumption (caustic soda, soda ash, lime)
- Absorber gas inlet temperature
- Absorber gas outlet temperature (after water wash)
- Absorber temperature profile
- Water make/loss from process
- Solvent make/loss from process
- Solvent flow
- Lean solvent loading
- Rich solvent loading
- Reboiler steam pressure (and temperature)
- Condenser temperature
- Condenser pressure
- Run duration
- Solvent performance degradation
- Limit on build-up of contaminants (heat stable salts, particulates, degradation compounds)
- Key gas compositions

The pilot facility is designed for operation in a semi-ballistic mode, by fixing several key parameters, and allowing the remainder to float during the test period. Filtration is not used, as understanding the rate and implications of the build up of degradation products and heat stable salts is an important aspect of the process.

E.4 GAS SAMPLING

The Pilot Plant is designed to allow easy access for gas analysis at several locations. Gas analysis is necessary to measure the CO_2 (and other gas species) concentration entering and leaving the pilot plant, as well as from various locations within the plant. This is required in order to determine the capture efficiency of the plant. The analysis system will also provide information on the fate of other flue gas components throughout the plant(SO_x/NO_x), the degree of solvent slip experienced, and will also be able to give an indication of solvent degradation through the detection of degradation by-products. A list of gas species that can be measured is provided in Table 1.

Table E.1. Species measurable with the PCC pilot plant.

Gas species	Max range	Unit
Water	45-50	Vol%
Carbon dioxide	100	Vol%
Carbon monoxide	500	ppmV
Nitrous oxide	100	ppmV
Nitrogen monoxide	700	ppmV
Nitrogen dioxide	700	ppmV
Sulphur dioxide	700	ppmV
Ammonia	500	ppmV
Hydrogen chloride	200	ppmV
Hydrogen fluoride	200	ppmV
Methane	100	ppmV
Ethane	50	ppmV
Ethylene	100	ppmV
n-Propane	100	ppmV
n-Hexane	50	ppmV
Formaldehyde	50	ppmV
Acetaldehyde	50	ppmV
Ethanol	50	ppmV
ethanolamine	800	ppmV
Ethylenediamine	50	ppmV
N-formylpiperazine	50	ppmV
Piperazine	500	ppmV

Gas analysis is performed using a Gasmet Fourier-Transform Infrared spectroscopy detection system. The system is capable of sampling gases from eight separate locations in series, examples of positioning are circled in red and labelled accordingly on the process flow diagram (PFD) of the plant provide in Figure 1. It is able to measure the concentration of several species concurrently. Seven of the analysis lines are placed at various locations around the plant as described below. The eighth line is used to monitor ambient gas concentrations.

Gas sample points are located as follows:

- Flue gas inlet to pre-treatment column (FPT GA1)

- Flue gas after pre-treatment column, before absorber column (FPT GA2)
- Above 2nd absorber packed section (ABS GA1)
- Above 3rd absorber packed section (ABS GA2)
- Above 4th absorber packed section (ABS GA3)
- At absorber exit (ABS GA4)
- CO_2 exit from stripping column (STR GA1)
- Ambient sample point (BOP GA1)

E.5 LIQUID SAMPLING

Chemical analysis by a titration method is used to determine the CO_2, MEA and free MEA concentration in the liquid samples. This determines the carrying capacity of the solvent, and can also be used to verify the plant CO_2 capture efficiency. Analysis of the liquid samples should also provide an indication of the water balance of the system
Liquid sample points are located as follows:

- Below 1st absorber packed section
- Below 2nd absorber packed section
- Below 3rd absorber packed section
- Rich solvent from ABS-TNK1
- Lean solvent entering absorber
- Lean solvent entering ABS-TNK2
- Below condensate packed section
- Below 1st stripper packed section
- Stripper condensate return line

E.6 CORROSION TESTING

Corrosion testing can be conducted at various locations around the plant. Access points have been included on both the absorber and stripping columns to allow placement of corrosion coupon test racks.
The column based locations of corrosion testing are:

- Below 1st absorber packed section
- Below 2nd absorber packed section
- Below 3rd absorber packed section
- In ABS-TNK1

- Below stripper condensate return
- Below stripper 1st packed section
- In STR-TNK1

Further pipe based corrosion coupon test racks can be installed at any flanged joint. Areas of interest for corrosion include:

- Downstream of the absorber column in the rich solvent
- Downstream of the stripping column in the hot lean solvent
- In the reflux return of the stripping column

E.7 DESCRIPTION OF PROCESS

The pilot plant has been designed to capture CO_2 using a STANDARD AMINE SOLVENT solution at a rate of 100 kg CO_2/hr. The design of the plant has been kept as flexible as possible to allow for the testing of other solvents, and some process modifications. The process essentially consists of three steps including pre-treating of the flue gas to remove particulates and cool the gas to the CO_2 absorption temperature, absorption of CO_2 in the aqueous amine solution and recovery of CO_2 from the spent amine solution. The PFD is presented below in Figure 7.

E.8 PRETREATING THE FLUE GAS

As shown in the process flow diagram, a slip stream of flue gas at approximately 135^{o}C and 95-100 kPa (absolute) enters the pre-treatment column where an alkali wash (caustic, pH around 9) is used to clean the flue gas and cool it to approximately 45^{o}C. The pre-treatment column is a single stage packed tower containing 2.7m of 1 inch stainless steel Pall rings. Demisting at the top of the pre-treatment column is done with a stainless steel fibre pad located above the packing. The lower end of the column is a liquid storage sump.

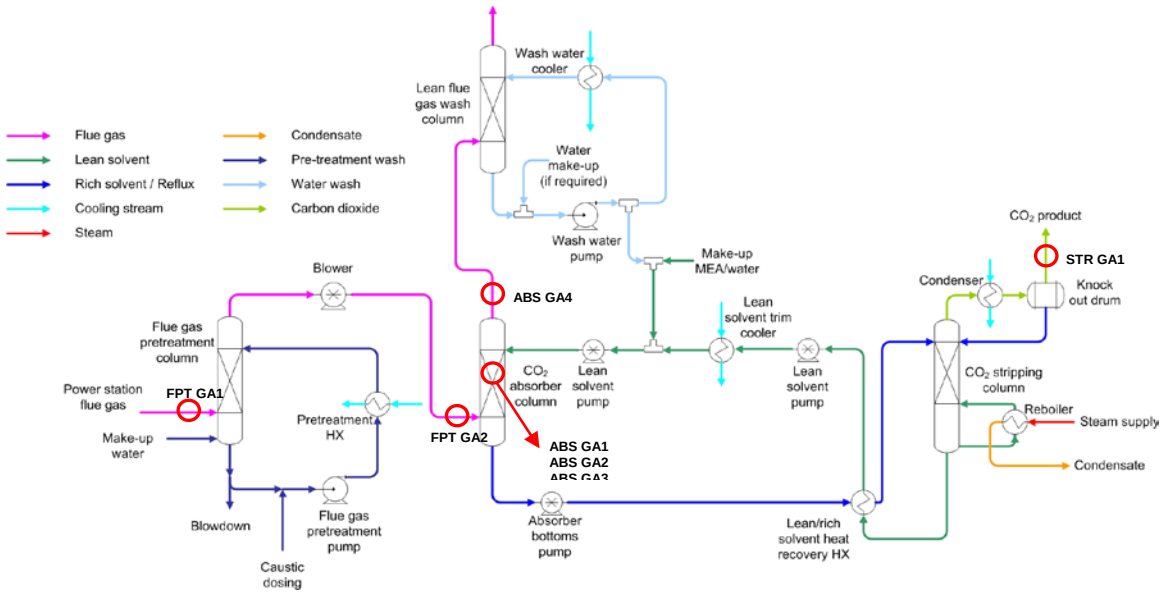


Figure 7. Plant process flow diagram.

Washing the process flue gas stream with the dilute caustic soda solution not only reduces its temperature but also reduces the NO_X and SO_X present in the flue gas. Blow down of caustic from the pre-treatment column reduces the build up of nitrate and sulfate salts of sodium in the solution and removes particulates removed from the flue gas. As the flue gas stream entering the pre-treatment column is not saturated, some water will be evaporated from the column as the gas is cooled. As a result make-up water will be added to the column at a rate of approximately 200 ml/min. Caustic is added to the warm spent wash solution leaving the pre-treatment column to maintain the pH at around 9. A pH measurement controls the dosing of caustic into the spent caustic solution. The caustic solution is then cooled to around 35^{o}C before returning to the pre-treatment column for re-use.

Raw water provides all of the cooling water requirements for the plant.

E.9 CO_2 ABSORPTION

The process flue gas leaving the pre-treatment column is at approximately 45^{o}C. The blower pumps the process gas leaving the pre-treatment column into the absorption column at around 105-110 kPa. The cleaned flue gas enters the absorption tower at the bottom end. The absorption section of the absorber column has four packed sections (structured packing), each 1.784m in height (7.136m total height), for intimate gas-liquid contacting.

The regenerated amine solvent cooled to 40^{o}C in the water cooled heat exchanger is pumped to the top of the absorption section for the counter-current gas-liquid contact. Since absorption of CO_2 by amines is an exothermic process, temperature rise in the packed section and higher temperature of amine solution leaving the absorption tower are expected. Temperature measurements are taken along the length of the column to monitor the temperature profile. Gas and liquid samples can be collected from in-between packed sections.

The overall pressure drop across the packed section is measured by a differential pressure transmitter indicator. This allows monitoring of the degree of liquid hold-up

occurring within the column. The lower leg of the differential pressure transmitter will be re-locatable to different positions on the column, so pressure drop across individual packed sections can be measured if desired. Any carried over amine is washed out of the CO_2 lean flue gas in the water-wash section of the absorption tower just above the packed sections for CO_2 capture. The wash water solution is collected at the bottom of the wash section in the column and returned to a holding tank for recycling to the water wash section of the absorption tower. Some excess wash water may be discharged through wash water blow down back to the solvent circuit prior to the absorption column

The spent amine solvent solution loaded with the dissolved CO_2 is pumped out of the absorber column, through the lean/rich heat exchanger, and into the stripping column for regeneration. Stainless steel solvent pumps are used to remove the solvent from the bottom of the column. The speed of the pump is controlled to a level set point to maintain a liquid seal at the bottom of the column to prevent entrainment of flue gas into the plant pipe work.

The absorber column has an integral water wash stage in the upper column section. Wash water is circulated using a small centrifugal pump to the top of the wash section via a water cooled heat exchanger to reduce the lean flue gas to close to the coolant temperature. The lean flue gas is then returned to the flue gas duct. It is intended to minimise changes to solvent concentration by water make/water loss to the solvent by maintaining both the pre-treatment column and the absorber top temperatures at a temperature that approaches the coolant temperature.

E.10 CO_2 RECOVERY

The CO_2 recovery step is carried out in the stripping column. This column has two packed sections of structured packing for gas-liquid contact (3.58m each, 7.168m total packed height) and it is operated at 1 to 10 bar (absolute) pressure. The column pressure is maintained via a pressure control loop that regulates a valve on the CO_2 product stream.

The spent amine solvent leaving the CO_2 absorption section is heated from approximately 55^{o}C to around 100–110^{o}C by exchanging heat with the regenerated lean amine solvent leaving the CO_2 stripping column in the lean/rich heat exchanger. The now hot rich solvent stream enters the stripping column at the top of the first stripping packed section and trickles down the column, whereas the CO_2 and water vapour generated in the reboiler at the bottom of the column, rise up the column. The countercurrent gas-liquid contact through the column packing allows CO_2 to strip out of the hot spent amine solvent and flow to the overhead condenser while the regenerated amine solvent flows down the column where it is collected at the base of the column.

Water condensed in the overhead condenser is accumulated in the overhead reflux tank and returned to the stripping column in such a way that it fully irrigates a demister packed section at the top of the column, located just above the first stripping packed section. This demister acts as a water-wash section and pre-cools the CO_2 and water vapour before it reaches the overhead condenser. The condenser temperature, as measured by the temperature of the reflux, is maintained by controlling the flow of coolant to the condenser.

The pressure drop across the packed sections in the stripping column is measured by a differential pressure indicator transmitter. The lower leg of the differential pressure transmitter will be re-locatable to different positions on the column, so pressure drop across individual packed sections can be measured if desired. Temperature transmitters are used to measure the temperature along the length of the column.

A dedicated steam boiler supplies saturated medium pressure steam on the shell side of the reboiler to drive the CO_2 stripping operation. The steam condensate accumulated in the reboiler is returned to the steam boiler via a holding tank.

The regenerated amine solvent leaving the stripping column is first cooled from approximately 115^{o}C to around 65^{o}C in the lean/rich heat exchanger, and is then further cooled down to 40^{o}C in the lean solvent trim cooler. The cooled regenerated solvent is collected in a holding tank before being recycled to the absorption column.

A pressure relief valve is located at the base of the column.

E.11 PILOT PLANT ENGINEERING DESIGN

The pilot plant is designed to test multiple solvents in several conditions. The materials selected are not consistent with those likely to be used at commercial scale. In order to be certain that the plant will be able to run reliably and safely with all trial solvents and at all conditions, process piping and columns have been constructed primarily in 316 stainless steel. Conditions of operation include for instance:
a flue gas flow rate of 595 kg/hr or 680 Am^3/hr and velocity of approximately 25 m/s and circulation of up to 600L of solvent and 150L of caustic wash.

Corrosion coupons placed around the plant throughout the duration of operating will be able to provide information relating to the suitability of metals used more commonly at the commercial scale. Figure 9 provides an isometric layout of the PCC pilot plant.

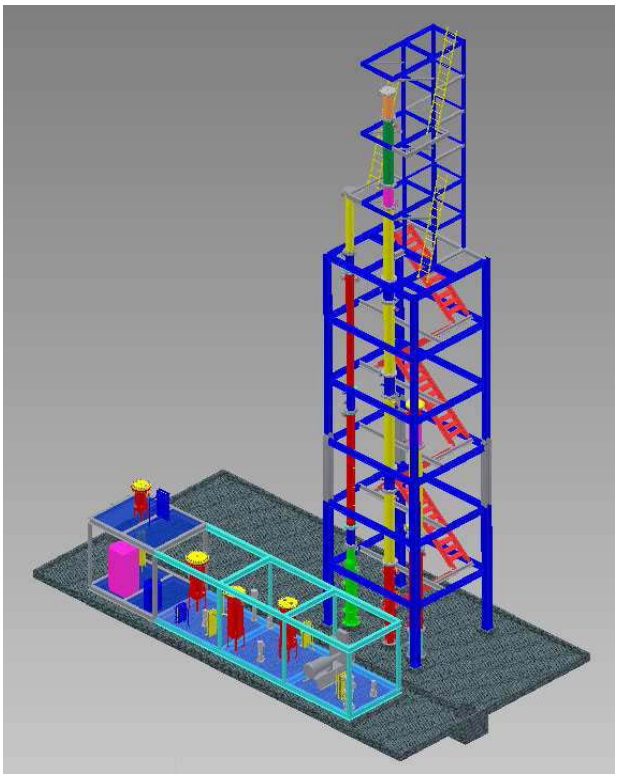


Figure 8. Isometric pilot plant diagram.

E.12 ENVIRONMENT AND SAFETY

CO_2 capture using solvents has several safety and environmental risks related to but not limited to the following:

- Potential of emissions or spills of solvent.
- Risk associated with the handling of solvent in maintenance or change out.
- Risk due to leakage of pressurized solvent or coolant.
- Risk due to the use of pressurised steam.
- Risk associated with the use of ladders to access the upper parts of the pilot plant.
- Risk from falling tools or other objects.
- Hot materials and surfaces.

All risks associated with this pilot facility have been addressed in line with Tarong Energy site protocols and procedures.

The pilot plant design incorporates a number of active and passive features, which will minimise these risks and their impacts, and include:

- Comprehensive control by PLC.
- Heavy construction with relief vents to withstand the over pressure from a HP steam leakage.
- A default map of operating conditions will be developed during commissioning to provide default settings in the event of failure of monitoring equipment.
- Provision of sufficient alarms and interlocks to ensure safe operation of the plant including strategies for partial, controlled and emergency shutdown sequences.
- Provision has been made for isolation valves, safety relief valves, drain valves, check valves strainers in order to allow safe operation and easy maintenance of the plant