Identification and monitoring of byproducts generated from an MEA absorbent during post-combustion CO_2 capture (PCC) from brown coal flue gases

A thesis submitted to the
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Doctor of Philosophy

by
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Abstract

During post-combustion capture (PCC) of CO_2, amine based absorbents undergo undesirable reactions which increase human and environmental impacts (due to emission and disposal of amine absorbents and degradation products), as well as operational and maintenance costs (due to amine consumption and corrosion). This thesis describes: (a) the degradation of a 30% (w/w) aqueous MEA absorbent during a six month campaign at CSIRO's PCC pilot plant located at AGL's Loy Yang brown coal-fired power station; (b) the chemical and physicochemical factors that are likely to affect the amine degradation; and (c) provides recommendations for technologies and strategies for monitoring and managing amine condition.

The aims and objectives of this thesis are defined in chapter 1. The samples of 30% (w/w) aqueous MEA absorbent from a CSIRO PCC pilot plant are crucial for the research presented in this thesis, and for this reason, the background of the sample set is also described in chapter 1. Chapters 2-7 contain publications that have been published in or submitted to respected peer-reviewed journals.

Chapter 2 contains a literature review that was published in *Environmental Science and Technology* during 2012. This literature review considers reasons for the consumption of amine during PCC (including oxidative degradation and carbamate polymerisation), other aspects of amine management (including fly ash, foaming, corrosion and amine reclamation), and environmental management (including nitrosation, atmospheric emissions, waste management). This publication is followed by a brief review of the relevant literature that has been published since 2012.

Chapter 3 describes the development, validation and use of a GC-FID method for quantification of MEA concentrations in the samples from a CSIRO PCC pilot plant. The MEA concentrations measured using GC-FID were statistically equivalent to the MEA concentrations measured by acid-base titration, which is the industry standard method. Importantly, this GC-FID method could be used to measure the concentrations of individual species in blended amine absorbents.

Chapter 4 uses spectroscopic and elemental methods to: characterise the changes in the organic structure and physiochemical environment of the MEA absorbent; and to evaluate potential methods for on- or at-line monitoring of MEA degradation during PCC. UV-Vis was identified as an effective on- or at-line technique for monitoring the production of N-(2-hydroxyethyl)imidazole (HEI), an oxidative MEA degradation product.

Chapter 5 investigates the processes responsible for the accumulation of inorganic anions, cations and metals in the MEA absorbent. The results obtained in this chapter demonstrate that fly ash was the most significant source of cations and indicates that oxidative degradation was a more significant source of heat-stable salts (HSS) than SO_x and NO_x from the flue gas. A potential change in corrosion mechanisms was identified from the change in ratios of iron, chromium, manganese and nickel concentrations and a rapid increase in the iron concentration was measured after the tenth sampling event.

To enable the quantification of organic degradation products other than organic acids, two sample preparation methods are described and validated in chapter 6. The cation exchange, derivatisation and GC-MS method was used to investigate the changes in the concentrations of organic degradation products during a pilot scale PCC campaign. These changes are discussed in chapter 7 and confirm that HEI is a suitable marker for oxidative degradation of MEA. The results in chapter 7 also suggest that the difference in ratios of organic acid concentrations at different PCC pilot plants may be due to the influence of operating parameters on the reaction pathways. This chapter also identifies coinciding discontinuities or disturbances in (a) the concentration profiles of all organic degradation products excluding the organic acids; and (b) the ratio of transition metal concentrations and increase in iron concentration. Two possibly related explanations provided for these changes are: (a) a decrease in the alkalinity due to the accumulation of HSS; and (b) the oxidation of residual aldehydes and/or sulphite during extended periods of absorbent storage prior to the last three sampling events.

Overall, the information presented in this thesis provides valuable insight into: (a) the rates of different amine degradation pathways; (b) accumulation rates of flue gas and corrosion byproducts during pilot-scale PCC; and (c) enabled the identification of oxidative degradation of MEA and accumulation of iron due to corrosion as the two most significant issues for managing amine condition during PCC.

General declaration

In accordance with Monash University Doctorate Regulation 17.2 Doctor of Philosophy and Research Master's regulations the following declarations are made:

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes two original papers published in peer reviewed journals and four unpublished publications. The core theme of the thesis is the degradation of the aqueous MEA absorbent sampled from CSIRO's post-combustion capture (PCC) of CO_2 pilot plant at Loy Yang. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the School of Applied Sciences and Engineering, Faculty of Science under the supervision of Prof. Samuel B. Adeloju, Dr T. Vincent Verheyen, Dr Erik Meuleman and Prof Alan L. Chaffee.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

In the case of chapters 2-7, my contribution to the work involved the following:

Table 1. Summary of the candidate's contribution to published works included in this thesis

Thesis chapter	Publication title	Publication status	Nature and extent of candidate's contribution
2	Towards commercial scale post-combustion capture of CO_2 with monoethanolamine solvent: Key considerations for solvent management and environmental impacts	Published	Defined the scope of the review. Wrote the initial draft, managed the revision process and incorporated changes, corrections and comments from the co-authors into the manuscript.
3	Quantification of aqueous monoethanolamine concentration by gas chromatography for post-combustion capture of CO_2	Published	Defined the aims and scope of the paper and experimental work. Conducted all the experimental work (except for 14 titration measurements). Wrote the initial draft, managed the revision process and incorporated changes, corrections and comments from the co-authors into the manuscript.

4	Evaluation of methods for monitoring MEA degradation during pilot scale post-combustion capture of CO_2	Submitted*	Defined the aims and scope of the paper and experimental work. Conducted all the experimental work with the exception of the NMR analyses. Wrote the initial draft, managed the revision process and incorporated changes, corrections and comments from the co-authors into the manuscript.
5	Primary sources and accumulation rates of inorganic anions and dissolved metals in a MEA absorbent during PCC at a brown coal-fired power station	Submitted*	Defined the aims and scope of the paper and experimental work. Conducted all the experimental work. Wrote the initial draft, managed the revision process and incorporated changes, corrections and comments from the co-authors into the manuscript.
6	Comparison of sample preparation methods for the GC-MS analysis of monoethanolamine (MEA) degradation products generated during post-combustion capture of CO_2	Submitted*	Defined the aims and scope of the paper and experimental work. Conducted all the experimental work. Wrote the initial draft, managed the revision process and incorporated changes, corrections and comments from the co-authors into the manuscript.
7	Characterisation of MEA degradation during pilot scale post-combustion capture of CO_2 at a brown coal-fired power station by GC/MS	Submitted*	Defined the aims and scope of the paper and experimental work. Conducted all the experimental work (except for the additional ion chromatographic analysis of 3 samples). Wrote the initial draft, managed the revision process and incorporated changes, corrections and comments from the co-authors into the manuscript.

*Submitted to CSIRO for internal peer-review prior to submission to a journal.

Although I conducted almost all of the laboratory work (including the development and adaptation of analytical methods; and troubleshooting and maintenance of the analytical instruments), I depended heavily on the assistance, advice and experience of my supervisor, Vince Verheyen. I was also assisted by Peter Nichols of Monash University (for NMR analyses and interpretation of the NMR spectra); Issac Rogers and Bart Clereen of MEP Instruments (for the analysis of three samples by ion chromatography); and various instrument technicians and engineers of Shimadzu Analytical and Measuring Instruments, Agilent Technologies, and Bruker (for advice and assistance during maintenance and troubleshooting). I am also indebted to CSIRO for allowing me to collect and analyse a set of degraded 30% (w/w) aqueous MEA samples from their PCC pilot plant at Loy Yang.

I have not renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis. Chapter structure and the formatting of tables and figures are in accordance with the requirements of the journals to which manuscripts have been submitted. Therefore, there are some formatting differences between chapters.

Signed: A. Reynolds

Date: 31-March-2015

Acknowledgements

I am grateful for the generous and valuable contributions of my supervisors, colleagues and collaborators toward the preparation of this thesis. I am also thankful for the financial support from a Brown Coal Innovation Australia (BCIA) research scholarship, an Australian Postgraduate Award scholarship from Monash University, and support from AGL Loy Yang.

I am particularly grateful of the valuable assistance from my supervisors in the following areas: the art of scientific writing (Sam Adeloju); the use, maintenance and troubleshooting of analytical equipment (Vince Verheyen); the wider needs, perspectives and focuses of the international PCC research community (Erik Meuleman from CSIRO); and general insightful advice (Alan Chaffee). A special acknowledgment is due to all the CSIRO personnel who made this research project possible by (a) operating and maintaining the pilot plant at Loy Yang; and/or (b) providing generous access to samples and data. I am also thankful for Jo-ann Larkin's generous and practical advice regarding the use and interpretation of statistical analyses.

Abbreviations

AA	Acetyl derivative; Acetic anhydride
AEHEIA	N-(2-aminoethyl)-N’-(2-hydroxyethyl)imidazolidinone (AEHEIA)
AMP	2-amino-2-methyl-1-propanol
ATR-FTIR	Attenuated total reflectance – Fourier transform infrared spectroscopy
BHEOX	N,N'-bis-(2-hydroxyethyl)-oxamide
CCS	Carbon capture and storage
DEA	Diethanolamine
Dehyd.	Dehydration (with rotary evaporation and molecular sieves)
GC	Gas chromatography
GC/FID	Gas chromatography with flame-ionisation detection
GC/MS	Gas chromatography with mass spectrometry detection
HEA	N-(2-hydroxyethyl)acetamide (HEA)
HEEDA	N-(2-hydroxyethyl)ethylenediamine
HEF	N-(2-hydroxyethyl)formamide
HEGly	N-(2-hydroxyethyl)glycine
HEHEAA	N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide (HEHEAA)
HEI	N-(2-hydroxyethyl)imidazole
HEIA	N-(2-hydroxyethyl)imidazolidinone
HEO	N-(2-hydroxyethyl)-2-oxoacetamide
HEPO	N-(2-hydroxyethyl)piperazin-3-one
HES	N-(2-hydroxyethyl)succinimide
HHEA	2-hydroxy-N-(2-hydroxyethyl)acetamide 8 (HHEA)
HPLC	High performance liquid chromatography
HPLC/MS	High performance liquid chromatography with mass spectrometry detection
HSS	Heat-stable salt(s)
IC	Ion chromatography; Inorganic carbon (a component of TOC)
ICP-OES	Inductively coupled plasma with optical emission spectroscopy detection

LLE	Liquid-liquid extraction
MEA	Monoethanolamine (2-aminoethanol)
MD	Mean deviation
MDL	Method detection limit
MDEA	Monodiethanolamine
MMEA	N-methyethanolamine
MS	Mass spectroscopy; Mass spectrum
NMR	Nuclear magnetic resonance
NOE	Nuclear Overhauser effect
OZD	2-oxazolidone
PCC	Post-combustion capture (of CO_2)
PQL	Practical quantitation limit
Pz	Piperazine
RSD	Relative standard deviation (%)
SCX	Strong cation exchange
SPE	Solid-phase extraction
TFAA	Trifluoroacetyl derivative; Trifluoroacetic anhydride
TC	Total carbon
TOC	Total organic carbon
UV-Vis	Ultra-violet and visible light spectroscopy

Chapter 1: Introduction

This chapter presents the aims and objectives of this thesis; describes the structure of this thesis; and provides a description of the sample set that is described in this thesis.

1.1 Aims and objectives

The research presented in this thesis addresses some of the needs identified by the literature review presented in chapter 2. The aims of this thesis are to:

A. Detect and identify trace components formed in monoethanolamine (MEA) absorbents during the PCC process and determine which reaction pathways are active in CSIRO's pilot plant at Loy Yang

B. Determine which reaction pathways have the most significant influence on the condition of the MEA absorbent and identify chemical markers for solvent damage

C. Develop strategies for monitoring and managing MEA absorbent condition. If possible, develop a conceptual design for a novel on-line device to maximize the technical and environmental performance of PCC plants worldwide

In order to achieve these aims, the seven objectives listed below were defined. The sample set that satisfies the first objectives is described in section 1.2. Each of the remaining objectives are directly addressed in chapters 3-7 of this thesis.

i. Obtain a set of samples of a MEA absorbent during a pilot-scale PCC campaign
ii. Develop a method that is capable of measuring MEA concentrations in the presence of heat-stable salts
iii. Use established spectroscopic and elemental techniques to characterise the changes in the composition of the MEA absorbent during the pilot PCC campaign
iv. Measure the accumulation of inorganic anions, cations and metals during the pilot PCC campaign
v. Develop at least one method for detecting and identifying trace organic components in the MEA absorbent
vi. Measure and compare the production of organic acids and other organic degradation products during the pilot PCC campaign
vii. Identify individual or classes of amine degradation products that are suitable markers for on-line or at-line monitoring
viii. Select and evaluate analytical techniques that are suitable for on-line or at-line monitoring of MEA degradation

1.2 Description of the sample set

In Australia, the Commonwealth Scientific and Industrial Research Organization (CSIRO) operates three pilot scale PCC plants at coal-fired power stations. The batch of 30% (w/w) aqueous MEA absorbent sampled for this thesis was used for CO_2 capture in two of these pilot plants. One pilot plant is located at Stanwell's 1400 MW black coal-fired power station at Tarong Queensland. This pilot plant has been used to investigate innovative amine based absorbents and novel process configurations with black coal flue gas. The second pilot plant was constructed at AGL's Loy Yang

2210 MW power station in Victoria during 2008. The pilot plant at Loy Yang has been used to test different amine based absorbent systems using brown coal flue gas. The pilot plant at Loy Yang is designed to separate 1000 t CO_2 / year from brown coal flue gas and is operated during working hours each day.

A batch of 30% (w/w) aqueous MEA absorbent was prepared and used to capture CO_2 at the PCC pilot plant at Tarong from the 2nd of December 2010 to the 30th of May 2011. During this time, novel process configurations and corrosion were investigated (Cousins et al., 2012; Cousins et al., 2013). The absorbent was then removed from the pilot plant, transferred to a plastic intermediate bulk container (IBC) and stored for 18 months prior to use at the PCC pilot plant at Loy Yang.

Twelve samples of this absorbent were obtained during the use of this absorbent at CSIRO's PCC pilot plant at Loy Yang between the 2nd of August 2012 and the 15th of January 2013. CSIRO conducted a concurrent investigation (Azzi et al., 2014) into the atmospheric emissions from this pilot plant campaign and this research. The only overlaps between these two projects were: (a) sub-samples of seven absorbent samples were provided to CSIRO for use in their research project; and (b) CSIRO provided the MEA concentration data measured by acid-base titration. The MEA concentration data provided by CSIRO was used to validate the GC-FID method in chapter 3.

During this PCC campaign, no chemicals or MEA other than water were added to the MEA absorbent. The absorbent did not contain anti-corrosive or oxidation inhibitor additives. The MEA concentration was monitored by acid-base titration by the pilot plant operators daily and, when necessary, water was added to the balance tank to maintain a consistent MEA concentration. Each sample was obtained during normal operation of the PCC pilot plant from a sampling port located between the lean absorbent storage tank and the CO_2 absorber system. Samples were collected in high-density polypropylene bottles which had been acid washed, rinsed with reagent grade water and dried at 50°C. After collection, the samples were immediately transferred to the laboratory and sub-sampled into acid washed bottles for metals analysis. All samples and sub-samples were stored at -20°C in the dark. Samples of the caustic absorbent used in the flue gas pre-treatment column were also obtained at each sampling event. These caustic absorbent samples were treated the same way as the absorbent samples but, they are only referred to in chapter 5. An additional sample of the MEA absorbent was taken from the IBC prior to the commencement of the PCC campaign at Loy Yang. This sample was also treated in the same manner as the other samples and is referred to in chapter 7.

In addition to the sampling of the 30% (w/w) aqueous MEA absorbent, CSIRO's data logging system and the date and time of each sampling event were used to determine: (a) the number of hours that the PCC pilot plant at Loy Yang had been operating using this absorbent; and (b) the mass of CO_2 that had been captured by this absorbent at Loy Yang. The operating hours were defined as the number of hours the flue gas flow rate was greater than zero and the mass of CO_2 captured was calculated from the flow rate of the gas exiting the CO_2 desorber, downstream from the water vapour condenser. The concentrations of ammonia, MEA and some other organic degradation products emitted from the absorber system are measured using an IR analyser. However, the calibration of this analytical method has not been reliable in the past, and for this reason, this data was not included in this thesis.

The twelve samples of the PCC absorbent were collected at regular intervals (approximately each fortnight, depending on the regularity of pilot plant operation), enabling the trends of organic compounds, inorganic anions, metals, cations and other parameters to be investigated. The prior use of this MEA absorbent for PCC of CO_2 ensured that the trends measured during the PCC campaign at Loy Yang were not influenced by impurities in freshly manufactured MEA. Chapter 4 clearly shows that the MEA degradation observed during this PCC campaign was: (a) comparable to degradation measured during other pilot-scale PCC campaigns around the world; and (b) severe enough to adversely impact the operation of the PCC pilot plant at Loy Yang. For these reasons, this set of twelve MEA absorbent samples was suitable for the investigation of the accumulation of inorganics, metals and cations as well as the production of organic degradation products during this pilot scale PCC campaign.

1.3 Structure of the thesis

Chapters 2-7 each contain either a published peer-reviewed paper, or a manuscript of a paper that has been submitted for peer-review and publication by a respected academic journal. Chapters 3 and 5 describe the development and validation of gas chromatography (GC) methods. The GC-FID (gas chromatography with flame ionisation detection) method for the quantification of MEA presented in chapter 2 was used to measure the concentration of MEA in each sample and these values are used in the statistical analyses in the following chapters. The GC-MS (gas chromatography with mass spectrometry detection) method described in chapter 6 was used to measure the semi-volatile organic compounds (SVOCs) in each sample and the results of these analyses are discussed in chapter 7. Although chapters 3 or 6 do not directly address the aims of this thesis, the need for these methods is recognised in objectives ii and v of this research. These methods also meet an important need for reliable methods for the identification and quantification of organic degradation products in MEA. These methods are also amenable to adaption to the analysis of organic degradation products in other amine based aqueous absorbents and other PCC process or waste streams.

Chapter 4: Monitoring amine degradation directly addresses objectives iii and Viii as well as contributing to aim C and objective vii. Aim C and objective vii are completed in chapter 6. *Chapter 5: Accumulation of metals and inorganics*, directly addresses objective iv of this research and contributes to the achievement of aim B. *Chapter 7: Oxidative degradation and carbamate polymerisation of MEA* contributes to all three aims and addresses objectives vi and vii. The final chapter (*Chapter 8: Conclusions and future directions*) discusses the outcomes of each aim and provides recommendations for the further research that is needed to enable the development of effective strategies and technologies that will enable the operation of PCC systems with minimal adverse impact on human health and the environment as well as minimising the economic cost of amine reclamation and replacement.

Chapter 2: Literature review

Towards commercial scale post-combustion capture of CO_2 with monoethanolamine solvent: Key considerations for solvent management and environmental impacts

A literature review that has been published in *Environmental Science and Technology* is included in this chapter. This publication is followed by a brief review of the research published in peer-reviewed journals since 2012. The full reference for this publication is:

Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Meuleman, E., Feron, P., 2012. Towards Commercial Scale Postcombustion Capture of CO_2 with Monoethanolamine Solvent: Key Considerations for Solvent Management and Environmental Impacts. Environmental Science & Technology 46, 3643-3654.

Three minor errors have been identified in this review since publication: page 3, main text paragraph 2 of the main text, sentence 1 should be “The use of alkaline aqueous amine solvents for separating acidic gases from ~~neutral~~ natural gas was first…”; page 9, paragraph 8, sentence 2 should be “Distillation removes suspended solids (such as residual fly ash), dissolved inorganics such as dissolved metals from corrosion ~~for~~ or fly ash)…”; and page 11, paragraph 5, sentence 2 should be “Measurement of the corrosion rates of ~~314~~ 316 stainless steel at that pilot scale…”

Declaration for Thesis Chapter 2

Declaration by candidate

In the case of Chapter 2, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Defined the scope of this literature review in this area, wrote the initial draft of the paper and coordinated feedback and comments from all authors.	80

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
T. Vincent Verheyen	Valuable advice on the structure, content and presentation of the manuscript.	N/A
Samuel B. Adeloju	Valuable advice on the structure, content and presentation of the manuscript. Co-ordinated submission and revision of the article	N/A
Erik Meuleman	Valuable input into the original scope of the literature review and valuable input into initial and final drafts	N/A
Paul Feron	Valuable input into final drafts	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature	A. Reynolds	**Date** 31-Mar-15
Main Supervisor's Signature		**Date** 31/3/15

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

Environmental Science & Technology
Critical Review
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Towards Commercial Scale Postcombustion Capture of CO_2 with Monoethanolamine Solvent: Key Considerations for Solvent Management and Environmental Impacts

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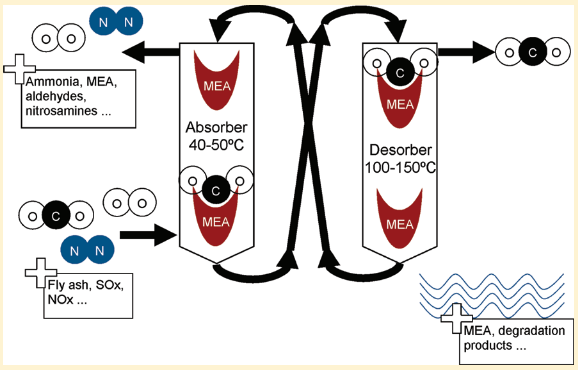
ABSTRACT: Chemical absorption with aqueous amine solvents is the most advanced technology for postcombustion capture (PCC) of CO_2 from coal-fired power stations and a number of pilot scale programs are evaluating novel solvents, optimizing energy efficiency, and validating engineering models. This review demonstrates that the development of commercial scale PCC also requires effective solvent management guidelines to ensure minimization of potential technical and environmental risks. Furthermore, the review reveals that while solvent degradation has been identified as a key source of solvent consumption in laboratory scale studies, it has not been validated at pilot scale. Yet this is crucial as solvent degradation products, such as organic acids, can increase corrosivity and reduce the CO_2 absorption capacity of the solvent. It also highlights the need for the development of corrosion and solvent reclamation technologies, as well as strategies to minimize emissions of solvent and degradation products, such as ammonia, aldehydes, nitrosamines and nitramines, to the atmosphere from commercial scale PCC. Inevitably, responsible management of aqueous and solid waste will require more serious consideration. This will ultimately require effective waste management practices validated at pilot scale to minimize the likelihood of adverse human and environmental impacts from commercial scale PCC.



1. INTRODUCTION

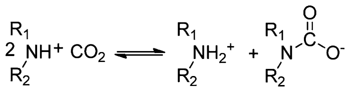
Post combustion capture (PCC) and storage of CO_2 is widely recognized as an important mitigation technology for reducing anthropogenic CO_2 emissions.[1,2] Various technologies have been considered for this purpose and future challenges in this area have been recently reviewed.[3] The most advanced and currently accepted PCC technology for coal-fired power stations is chemical absorption with aqueous amine solvents.[1,4,5] This system is effective at low CO_2 partial pressures (typically 13−14% for coal-fired power stations) because the acidic CO_2 reacts chemically with the alkaline aqueous amine solvent.[3]

The use of alkaline aqueous amine solvents for separating acidic gases from neutral gas was first patented in the 1930s[6] and extensive experience has been developed for its use in natural gas, coking, and ammonia synthesis industries.[7] Design, operation, and maintenance guidelines for separating acidic gases from natural gas have been published by Kohl and Nielsen.[7] The two major costs associated with operating alkanolamine based natural gas purification plants are corrosion and amine solvent degradation.[7−10]

Being the key component of chemical absorption PCC, the development of solvents is a major area of research.[11−14] The ideal solvent has a high CO_2 absorption capacity and reacts rapidly and reversibly with CO_2 with minimal heat requirement.[11] The solvent should also have good oxidative and thermal stability, low vapor pressure, low toxicity, low flammability, and be readily available at low cost.[15]

Aqueous amines are the most common solvents for PCC and 30% monoethanolamine (MEA) is the industry standard, although superior performance can be achieved with some commercial amines.[11,16−18] During PCC, both primary and secondary amines react with CO_2 to form a carbamate and protonated amine, consuming approximately two mole of amine per mole of CO_2,[19] as shown in Scheme 1. Sterically

Scheme 1. Absorption of CO_2 by Primary or Secondary Amine to Form Carbamate:[5]


$$2\,R_1R_2NH + CO_2 \rightleftharpoons R_1R_2NH_2^+ + R_1R_2N{-}C(=O)O^-$$

For MEA, $R_1 = H$ and $R_2 = CH_2OH$

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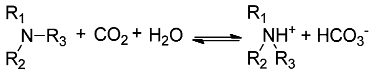
hindered and tertiary amines react with CO_2 to form of bicarbonate (Scheme 2) and consume only one mole of protonated amine per mole of CO_2 absorbed.[19,20] However, Scheme 1 is generally more rapid than Scheme 2[19] and primary and secondary amines are commonly used for pilot scale PCC despite their lower CO_2 capacity.[21−24]

Scheme 2. Absorption of CO_2 by Tertiary or Sterically Hindered Amine to Form Bicarbonate:[5]



$$R_1R_2N{-}R_3 + CO_2 + H_2O \rightleftharpoons R_1R_2R_3NH^+ + HCO_3^-$$

Other aqueous amines with similar CO_2 absorption rates but with lower capacity than MEA include 2-amino-2-methyl-1-propanol (AMP, sterically hindered primary amine), methyldiethanolamine (MDEA, tertiary amine), MMEA (N-methylethanolamine, secondary amine) and diethanolamine (DEA, secondary amine).[11] The cyclic diamine, piperazine has higher CO_2 capacity and absorption rates than MEA,[11] but its use is hampered by solubility constraints.[16]

As coal-fired power station flue gases typically contain percent levels of oxygen as well as SO_x and fly ash, solvent degradation and corrosion are serious concerns for PCC.[3] Recent studies have demonstrated that both solvent degradation and corrosion rates are dependent on the dissolved oxygen concentration.[25−29] A variety of oxygen scavengers and corrosion inhibitors have also been investigated in laboratory trials but many additives accelerate oxidative degradation or form heat stable salts with MEA.[29−34]

Besides the monetary costs of corrosion and solvent degradation, the human and environmental impact of substituting CO_2 emissions with amine solvent and degradation products is poorly understood. Preliminary predictions of human and environmental impact of gaseous, aqueous and solid wastes likely to be produced during commercial scale MEA-based PCC vary from mild impacts[35] to increased fresh water and terrestrial ecotoxicity.[36,37] However, very little information is available regarding the formation, emission, atmospheric chemistry, and ecotoxicity of solvent degradation products at the pilot or commercial scale.[37−40] Ultimately, it is essential to ensure PCC does not unwittingly create a human or environmental hazard while mitigating anthropogenic CO_2 emissions.

Although MEA degradation has been investigated extensively at the laboratory scale, few studies have taken the opportunity to validate laboratory based degradation despite the availability of pilot scale PCC from coal-fired power stations.[24,41−43] Degradation of other aqueous amines such as piperazine,[32,44] MMEA[45] and MDEA[31] has been investigated at the laboratory scale but the strongest emphasis has been on the MEA, the current industry standard solvent for PCC. The undoubted need for validation of laboratory scale studies at pilot scale is emphasized by fact that many of the major compounds detected in reclaimer bottoms and lean aqueous MEA at a commercial CO_2 capture facility at Trona, California have not been previously reported in laboratory scale MEA degradation.[43]

Recent reviews have addressed advances in technology, economics, and engineering models for aqueous amines PCC from coal-fired power stations.[3,42,46,47] In this review, the focus is on solvent consumption (degradation and evaporation), solvent management (corrosion, foaming, and reclaiming) and environmental management (solid and aqueous waste as well as emissions to atmosphere) for MEA-based PCC of CO_2 from coal-fired power stations. Although the development and evaluation of existing and novel solvents for PCC is ongoing, many of the factors pertinent to solvent consumption, solvent management and environmental risks identified in this review are relevant for many aqueous amine PCC solvents.[7,14]

2. SOLVENT CONSUMPTION

There are many opportunities for solvent consumption by chemical degradation as well as physical processes such as evaporation and droplet carryover during the PCC process. The intimate mixing of the amine solvent with flue gas containing oxygen, SO_x and fly ash, during CO_2 absorption is known to accelerate oxidative degradation.[23,24] Carbamate polymerization occurs during CO_2 desorption where the solvent experiences high temperatures (100−150 °C) and high CO_2 partial pressures.[48] Solvent is also lost at the outlets of both the CO_2 absorber and CO_2 desorber columns as vapor and aerosols, but most of this solvent can be recovered by scrubbing the lean flue gas and CO_2 product streams with water.[24,37] The relative contributions of these MEA consumption pathways have been estimated for a natural gas power station by Veltman et al.[37] and are presented in Figure 1.

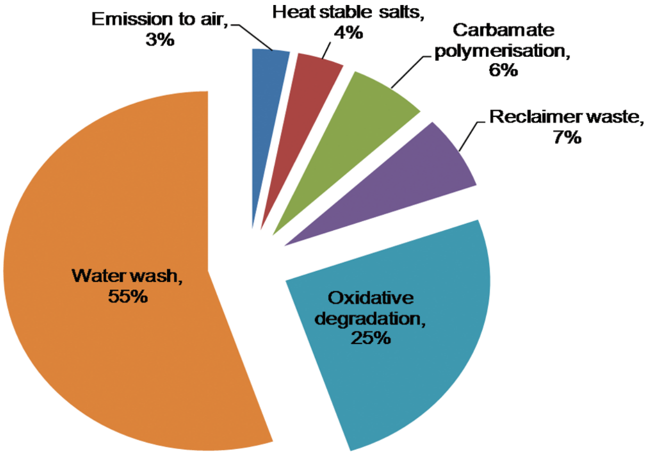


Figure 1. Estimated sinks of consumed MEA in a typical 420 MW natural gas combined cycle power station with PCC. Adapted from Veltman et al.[37].

The most significant loss of MEA is through evaporation from the absorber column, but approximately 95% of the evaporated solvent may be recovered by washing the CO_2 lean flue gas with water.[37] Water scrubbing also reduces the emission of other water-soluble volatile organic compounds (VOCs) such as oxidative degradation products which are also usually evaporated from the absorber column.[24,37] The water for scrubbing the CO_2 lean flue gas is usually recirculated with a small bleed to prevent accumulation of solvent and other VOCs.[21,23,24,37] This bleed can be used as PCC solvent makeup or treated as wastewater,[23,24,37] but it is extremely important to ensure that the solvent and degradation product emissions to atmosphere or wastewater from commercial scale PCC do not pose any harmful environmental and/or human health effect.

Oxidative degradation accounts for the next most significant MEA loss[37] and has been observed in PCC pilot plants operating at coal-fired power stations.[23,24] Carbamate polymerization and formation of heat stable salts are minor MEA degradation pathways but the products increase the severity of corrosion and foaming.[7,49,50] Thermal degradation of MEA can occur when solvent is reclaimed by distillation at or above 200 °C, but has not been observed during CO_2 desorption.[28] Thermal degradation is not included in this review because very little information is available in literature and solvents are not usually reclaimed during PCC pilot trials.[23,24,51] Reactions with fly ash and SO_x from the coal-fired power station flue gas are also known to consume MEA.[23,37,42,52,53]

2.1. Oxidative Degradation. Oxidative degradation of MEA solvent used for PCC of CO_2 from flue gas of coal-fired power stations is of particular interest because the flue gas typically contains 3−4% oxygen.[3] For this reason, PCC pilot plants based on the use of aqueous MEA for CO_2 removal from coal-fired power stations have shown considerable interest in measuring oxidative degradation products in treated flue gas,[23,24] CO_2 product[23,24] and used MEA solvent.[24] Laboratory scale experiments indicate that MEA oxidation rates are limited by oxygen mass transfer under typical PCC conditions.[28] Goff and Rochelle[28] estimated that oxidative degradation in a typical pilot plant absorber would consume 0.29−0.73 kg MEA/tCO_2 captured, which is within the range of MEA consumption rates reported for pilot plants (0.28 and 1.4 kg MEA/tCO_2 captured).[23,24] This clearly supports the argument that oxidative degradation is a significant contributor to solvent consumption during PCC operation.

Laboratory scale simulations are often used to investigate the effects of process variables such as CO_2 loading, SO_2, temperature, and the presence of transition metals on amine solvent degradation.[14,26−28,31,53−60] Most laboratory scale simulations aim to reproduce industrial absorber or desorber conditions by providing excess oxygen, high mass transfer rates and operating temperatures of 40−200 °C. Common laboratory equipment and conditions used to simulate degradation are summarized in Table 1. Most researchers have used either glass or stainless steel reaction vessels and high purity MEA and water. However, MEA is known to leach metals from stainless steel[45] and dissolved transition metals are known to catalyze free radical oxidative degradation mechanisms[28] and, hence, may increase degradation rates and influence oxidation mechanisms. The effects of impurities in industrial grade MEA and make up water are unknown and warrant further investigation.

During laboratory scale degradation studies, various gases such as oxygen, carbon dioxide, sulfur dioxide, and nitrogen dioxide are usually sparged[27,28,59] into aqueous MEA or delivered as either a stream of gas through the headspace,[31,60] or used to pressurize the headspace.[14,26,53−58] Pressurizing the headspace of a static closed system allows the system to come to an equilibrium and facilitates long reaction times,[54] while sparging or stirring maximizes the mass transfer rate.[28] A continuous gas stream more closely resembles the industrial process and is useful for online analysis of volatile products, such as ammonia,[27,28,59] amides, and gas consumption[60] by gas phase IR (infrared) spectroscopy.

A more sophisticated "integrated solvent degradation apparatus" (ISDA), included in Table 1, has been described in detail by Closmann and Rochelle.[31] The ISDA is a simplified laboratory scale CO_2 capture facility without the ability to desorb CO_2 and has been constructed to investigate the effects of temperature cycling on solvent degradation.[31] Carbon dioxide absorber conditions are modeled by stirring aqueous amine solvent in a glass, water jacketed vessel with a gas

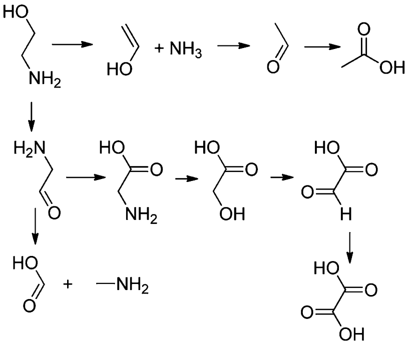
Table 1. Reported Laboratory Scale Oxidative Degradation

reactor type and material	gas delivery	MEA and water grades	temperature range (°C)	time span	sampling and analysis	reference(s)
10 mL stainless steel batch reactors or glass lined stainless steel batch reactors	none	not reported	100−150 °C convection oven	several months	IC, HPLC, MS	45,48
600 mL stainless steel autoclave, stirred	pressurized with desired gas mix	reagent or research grade (>99%) MEA, DI water	55−170 °C electrical heater and cooling water coil	multiple days to 3 weeks	liquid subsamples analyzed by HPLC, GC/MS, etc.; gas subsamples analyzed by GC/MS, and GC/TCD for permanent gases	26,53−58
100 mL stainless steel closed vessel, stirred at 250 rpm	Pressurized with desired gas mix	not reported	140 °C	15 days	final liquid samples analyzed by IC, NMR, and GC/MS	14
glass vessel, not stirred	Sparged with 5 L/min	low chloride and iron grade MEA	55 °C water jacket	Up to 8 h	product gas analyzed for ammonia by FTIR	27
1 L glass vessel, not stirred	Sparged with up to 8 L/min gas	low chloride and iron grade MEA, DI water	55 °C water jacket	8−17 h	product gas analyzed for ammonia by FTIR	28
glass vessel, agitated at 1450 rpm with stainless steel stirrer	Sparged with up to 8 L/min gas	500 mL low chloride and iron grade MEA, DI water	40, 55, and 70 °C water or silicon oil jacket	8−17 h	product gas analyzed for ammonia by FTIR	28,59
glass vessel stirred at 1400 rpm	100 mL/min or 7.5 L/min flow through headspace	not reported	55 °C water jacket	500 h (20 days)	product gas analyzed by FTIR; final liquid products analyzed by IC and HPLC	60
integrated solvent degradation apparatus (ISDA)	100 mL/min flow through headspace	not reported	absorber: 55 °C Desorber: 55 to 120 °C Water and silicon oil jackets	450 h (19 days)	final liquid samples analyzed by titration, IC, HPLC/MS, and GC/MS	31

mixture flowing through the headspace. Solvent is pumped from the bottom of this vessel through heat exchangers to a stainless steel thermal reactor.[31] Solvent returns through heat exchangers to the absorber vessel. MEA degradation in the ISDA has not been reported, but oxidative degradation of methyldiethanolamine (MDEA) was dependent on the temperature of the thermal reactor.[31] Hence, the effect of thermal cycling on MEA degradation warrants investigation.

Laboratory scale oxidative degradation trials[26,55] have identified an extensive list of degradation products. The most commonly reported oxidative degradation reactions are shown in Scheme 3, but much more extensive degradation pathways have been reported.[56] Volatile acids and aldehydes (e.g., formaldehyde, formate, acetylaldehyde, acetate, and oxalate), crown ethers and a wide range of nitrogen containing compounds (e.g., ethylamine, imidazole, pyrimidine, and uracil) form the bulk of other products reported from laboratory scale simulations.[26,55,56,60] However, as shown in Table 2, the major organic compounds present in reclaimer bottoms from a PCC plant of a coal-fired power station at Trona, California have not yet been reported as MEA degradation products in laboratory scale experiments.[43] As this is the only reported extensive characterization of solvent from a MEA based PCC, this observation highlights the need to validate laboratory scale simulations by incorporating suitable sampling and analytical regimes into current pilot scale PCC programs.

Scheme 3. Oxidative Degradation of MEA. Adapted from Bello and Idem.[26]



Major oxidative degradation products, such as ammonia, are commonly monitored online by gas phase IR as an indicator of real-time oxidative degradation rates during laboratory simulations and at PCC pilot plants.[27,28,60] Ammonia emissions accounted for approximately 30% of the MEA consumption (0.4 kg MEA/tCO_2 captured) at the CASTOR pilot plant at Esjberg (Denmark)[23] and all MEA consumption at a PCC pilot plant at a brown coal-fired power station in Niederaussem (Germany).[24] Other volatile oxidative degradation products, such as volatile acids and aldehydes, have been detected in the gas streams exiting the absorber and desorber columns of both the CASTOR and Niederaussem pilot plants. Acetate accounted for 71% of MEA consumption (0.21 kg MEA/tCO_2 captured) at the Niederaussem pilot plant.[24] While these results are variable, they suggest that the dominant MEA oxidation pathway in pilot scale PCC produces both ammonia and acetate from each MEA molecule (Scheme 3). Importantly, these results also confirm that oxidative degradation is a significant contributor to solvent degradation and consumption in PCC pilot plants.

Reaction of organic acids (such as formate and acetate) with MEA leads to formation of amides[23,61] which are also referred to as heat stable salts (HSS). It is important to minimize the formation and accumulation of HSS in PCC solvent because they reduce the amount of MEA available to absorb CO_2[61] and lead to increasing corrosion[49] and foaming.[62] Veltman et al.[37] estimated that 90% of volatilized organic acids and their precursor aldehydes are likely to be removed from the treated

Table 2. MEA Degradation Products Identified in Reclaimer Bottoms from a PCC Plant at Trona, California by Strazisar et al.[43] and Detection of These Compounds during Other Laboratory Simulations and Pilot Plant Trials

compounds identified in reclaimer bottoms at Trona California[43]	CAS number	source	reference(s) for lab simulations	reference(s) for PCC plant or pilot plant
N-formylethanolamine	627−45−2	oxidative degradation, condensation	60,61	43
N-acetylethanolamine	142−26−7	oxidative degradation, condensation	26,55,61	43
2-oxazolidone	497−25−6			43
N-(hydroxyethyl)-succinimide	18190−44−8	oxidative degradation, condensation	55,61	43
N-(2-hydroxyethyl)-lanthamide	5422−34−4			43
1-hydroxyethyl-3-homopiperazine	Not available			43
1-(2-hydroxyethyl)-2-imidazolidinone	3699−54−5	carbamate polymerization	26,48,55	24,43
1-hydroxyethyl-2-piperazinone	59702−23−7			43
4-hydroxyethyl-2-piperizinone	23936−04−1			43
3-hydroxyethylamino-N-hydroxy-ethylpropanamide	144236−39−5			43
2-hydroxyethylamino-N-hydroxyethylacetamide	Not available			43
ammonia	7664−41−7	oxidative degradation	27,28	23,24,43
acetic acid	34−19−7	oxidative degradation	60	24,43
propanoic acid	79−09−4			43
n-butyric acid	107−92−6			43
monoethanolamine	141−43−5	solvent		43
2,6-dimethyl-4-pyridinamine	3512−80−9			43
2-imidazolecarboxaldehyde	10111−08−7			43
1-methyl-2-imidazolecarboxaldehyde	13750−81−7			43

flue gas stream by water wash which may be returned to the working solvent. However, these estimates have not been confirmed at the pilot scale.

Formic, acetic, glycolic, succinic, and oxalic acids are known products of MEA oxidative degradation and exist in equilibrium with their amides in PCC solvent.[61] The MEA amides of formic and acetic acids, (N-(2-hydroxyethyl)formamide and N-(2-hydroxyethyl)acetamide respectively) have been reported in laboratory degradation experiments[26,55,60] and reclaimer bottoms from a CO_2 capture facility in Trona, California.[43] The MEA amide of succinic acid condenses to form the cyclic N-(2-hydroxyethyl) succinimide[61] which has also been reported in laboratory degradation experiments[26,55] and reclaimer bottoms.[43] The MEA glycolic acid amide (2-hydroxyglycolamide) has not been reported in literature but was found to form rapidly on mixing MEA and glycolic acid. N-(2-hydroxyethyl)-formamide, N-(2-hydroxyethyl)acetamide, 2-hydroxyglycolamide, and N-(2-hydroxyethyl)succinimide formed rapidly on mixing MEA and increased in concentration over 3−4 days before decreasing over 4−7 days.[61]

Unlike other organic acids, oxalic acid formed both N,N′-bis-(2-hydroxyethyl)oxamide and N-(2-hydroxyethyl)formamide when mixed with aqueous MEA.[61] As the time progressed the equilibrium shifted to favor N-(2-hydroxyethyl)oxamide (the partial amide of oxalic acid and MEA) over N,N′-bis-(2-hydroxyethyl)oxamide.[61] Furthermore, in the presence of oxygen, oxalate readily degraded to formate.[61]

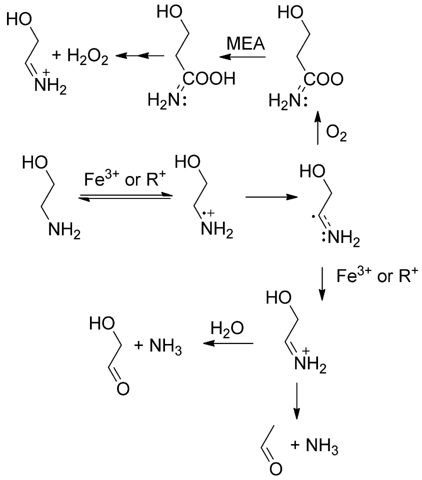
The cause of the shifts in equilibrium in the closed, temperature controlled system is yet to be fully understood and explained.[61] However, the partition between amides and amine-organic acid salts may influence the corrosivity of the solvent and, hence, could have a significant influence and effect on the design and utilization of a commercial scale PCC. Amides are known to hydrolyze in strong alkali,[60] thus indicating that pH changes could have influenced the equilibria of these reactions. Furthermore, as these reactions were conducted in stainless steel, which readily interacts with MEA and heat stable salts,[16] these interactions could have also influenced the equilibria. Dissolved metals are known to catalyze oxidative degradation, and this factor highlights the need for a careful choice of suitable material for the reaction vessels, in order to minimize uncontrolled variables in both laboratory and plant-based PCC systems.

2.1.1. Catalysis of Oxidative Degradation. The introduction of transition metals, such as copper,[28,33] iron,[27,28,33] vanadium[33] and a number of other metals are known to increase the rate of MEA oxidative degradation. In the presence of dissolved iron and copper, the oxidative degradation rates of MEA are limited by oxygen mass transfer and, thus, suggesting that metal catalysis may be an important oxidative degradation pathway.[28,60] Potential sources of dissolved transition metals in a PCC plant include fly ash, corrosion, and corrosion inhibitors[23] but the relative contributions are unknown.

An early study reported found 1−50 ppm of iron, copper, nickel, and vanadium in used MEA solvent from a CO_2 absorption plant used to clean the air in a nuclear submarine catalyzed oxidative degradation.[8] Also, iron (1.4 ppm), copper (0.2 ppm), and zinc (0.3 ppm) have been detected in the lean solvent from the PCC plant of a coal-fired power station.[43] While laboratory simulations indicate that metal catalyzed oxidative degradation may be important,[25,27,29,33] this has not been confirmed or refuted at the pilot scale. There is therefore an immediate need to determine whether or not dissolved transition metals from corrosion and fly ash are accumulating in solvent as part of current pilot PCC plant programs.

The presence of transitions metals are known to catalyze the formation of radicals such as $O_2^{\bullet}$, $OH^{\bullet-}$ and H_2O_2 in aqueous solution which may subsequently react with MEA, resulting in a number of degradation products as shown in Scheme 4.[27]

Scheme 4. Oxidation of MEA Catalysed by Fe^{3+} or Other Electron Acceptors Adapted from Chi and Rochelle[27]

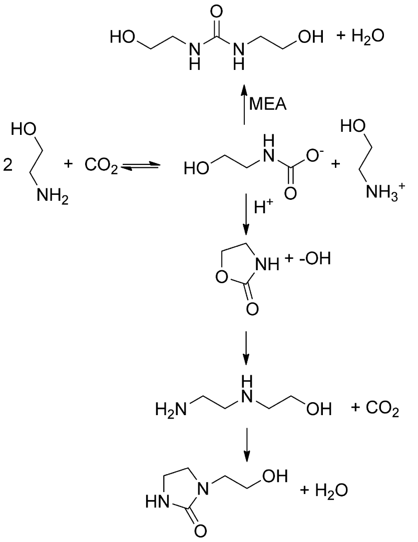


Ferrous (Fe(II)) and other reduced forms of transition metals are known to be rapidly oxidized by dissolved O_2.[27] However, it is difficult to differentiate between catalyzed and noncatalyzed MEA oxidation because both pathways produce ammonia and small organic acids such as formaldehyde.

2.2. Carbamate Polymerization. As the temperature in a typical chemical absorption based PCC plant desorber is typically between 100 and 150 °C,[48] there is a tendency for carbamates to polymerize in CO_2 desorber columns. Although carbamate polymerization is considered a minor pathway for MEA degradation during PCC,[37] there is some concern about the ability of carbamate polymerization products to act as strong chelators with the tendency to facilitate corrosion.[7] Under laboratory conditions, the rate of carbamate polymerization quadruples with every 17 °C increase in temperature or doubling of pressure and is linear with respect to reagent (MEA and MEA carbamate) concentration.[48] The temperature and pressure of CO_2 desorber columns are usually selected to balance the rate of carbamate polymerization and overall energy efficiency of the capture plant.[48]

Simulation of carbamate polymerization has been undertaken in laboratory conditions by using equipment and techniques described in previous sections and summarized in Table 1. The main carbamate polymerization reactions can be classified as *addition*, *imidazolidone formation or demethylation*, *dealkylation*, and *methylation*.[14] Scheme 5 summarizes the most commonly reported reactions of MEA. The major carbamate polymerization products of MEA are 1-(2-hydroxyethyl)imidazolidine-2 (HEIA), dihydroxyethylurea and N-(2-hydroxyethyl)ethylenediamine (HEEDA).[14,48] Also, the presence of 2-oxazolidone has been found in the reclaimer bottoms from a PCC plant at Trona, California,[43] but not identified in laboratory simulation of MEA degradation. This, again, highlights the need to validate laboratory simulations by appropriate pilot PCC plant programs before embarking on the development of commercial scale PCC.

Scheme 5. Carbamate Polymerization Reactions[14,26,48]



3. OTHER ASPECTS OF SOLVENT MANAGEMENT

The presence of high oxygen concentrations, fly ash and SO_x in coal-fired flue gas are likely to cause corrosion and erosion problems during operation of commercial scale PCC of CO_2. Common considerations in solvent management, such as foaming and solvent reclamation[7] are also important for operation of commercial scale PCC. The lack of accumulation of impurities in the solvent in pilot scale PCC plants[63] due to the relatively short operating times has not necessitated the reclamation of solvent.[23,24] However, the consideration of solvent reclamation will become necessary as the long-term stability and corrosivity of the solvent will become a significant issue in commercial scale PCC.

3.1. Fly Ash. By use of electrostatic precipitator and/or fabric filters[64] more than 99% of fly ash is usually removed from coal-fired power station flue gas, but many pilot scale PCC plants operate additional flue gas preconditioning columns.[21,23,24,51] Many pilot PCC plants also filter a slip stream of solvent through mechanical and carbon filters to prevent accumulation of residual fly ash particles.[23,24] In spite of these removals, low ppm levels of calcium and potassium found in lean MEA from a pilot PCC plant at a coal-fired power station in Trona, California were attributed to fly ash,[43] although makeup water may be another source of calcium and potassium.

The composition of fly ash in flue gas from coal-fired power plant is highly variable and typically contains the mineral and uncombusted carbonaceous components of coal.[65] Minerals such as silicates, sulfides, sulfates, carbonates, and chlorides[65] can contribute to erosion, whereas those of transition metals can catalyze oxidative degradation of MEA.[25,27,29,33] However, the extent to which fly ash can accumulate and impact on commercial scale PCC operation cannot be under-rated or ignored and, thus, warrant further investigation, particularly in relation to the much longer length of operation required for commercial scale PCC.

3.2. Foaming. The interaction between natural gas and amine solvents is known to often result in foaming which has been attributed to the carryover of condensed hydrocarbons and accumulation of organic acids.[7] However, no PCC pilot plants have reported the incidence of foaming in the open literature, possibly because of their relatively short operation times and the absence of condensed hydrocarbons in coal-fired power station flue gas. However, laboratory based studies have demonstrated that CO_2 loading, acidic degradation products, corrosion inhibitors, temperature and flow rates affect the foaming behavior of MEA.[62,66,67]

3.3. Corrosion. Metallic corrosion has been observed at MEA-based PCC plants at coal-fired power stations[63] and is exacerbated by the accumulation of heat stable salts (particularly oxalic acid) which are acidic, conduct electricity and chelate metals.[7] Both laboratory and pilot scale studies show that high temperatures, presence of oxygen, MEA concentration, the CO_2:MEA ratio and heat stable salts increase corrosion rates of metal in contact with aqueous MEA.[49,63,68,69] However, at the laboratory scale, MEA and CO_2 concentrations have a much more significant impact on the corrosion rates than the O_2 concentration.[63]

The corrosion rates of 1018 carbon steel have been measured at the CO_2 rich solvent inlets and CO_2 lean solvent outlets of the desorbers at the pilot PCC plants at Esbjerg coal-fired power station in Denmark and the International Test Centre at Regina (Canada).[63] The corrosion rates of 316 and 304 stainless steel coupons were below 5 μm/year in the same locations,[63] and these were deemed acceptable for structural purposes. However, MEA has been found to leach metals from 316 stainless steel[16] and this has a significant implication which may require sourcing of alternative materials for the large surface area of column packing in absorber and desorber columns in order to minimize catalytic oxidative degradation of MEA by dissolved transition metals.

Laboratory corrosion experiments have demonstrated that oxalic acid is more corrosive to 1018 carbon steel than formic, acetic, malonic, glycolic or succinic acid in 5 M MEA at a 0.2 mol CO_2/mol MEA at 80 °C.[49] Oxalate is known to chelate iron and disrupt the formation and stability of passive films on 1018 carbon steel.[7,49] Tanthapanichakoon et al.[49] suggested that oxalic acid also reduces oxidizing agents, which is consistent with the observation of rapid oxidation of oxalic acid to formate on mixing oxalic acid with aqueous MEA by Supap et al.[61] This is also consistent with lower corrosivity of formic, acetic, glycolic, and succinic acids[7,49] which did not cause oxidation when mixed with aqueous MEA.[61] Importantly, oxalic acid did not accelerate corrosion of 304 stainless steel, a common structural material for pilot PCC plants.[49,63] While stainless steels generally exhibit good corrosion resistance to organic acids, formic and oxalic acids are known to cause localized (pitting) corrosion.[70] The presence of halides also initiate pitting corrosion in stainless steels, particularly at neutral and alkaline pH.[70] Chloride has been measured in both lean solvent (0.16%) and reclaimer bottoms (4.9%) at a PCC plant of a coal-fired power station at Trona, California.[43] The presence of chloride was attributed to hydrochloric acid from coal combustion[43] which accumulated in the reclaimer. As metallic corrosion can be a significant source of transition metals for catalytic oxidative degradation, the possible cause and control of accumulation of organic acids, chloride and other halides in MEA warrants further investigation.

Corrosion inhibitors, such as $NaVO_3$ and $CuCO_3$, have been used to minimize corrosion,[68] but can also be sources of dissolved transition metals which may catalyze oxidative degradation of MEA. Sodium metavanadate ($NaVO_3$) was not effective during the corrosion trials at the Esbjerg coal-fired power station in Denmark[63] and an order of magnitude increase in MEA degradation rates were observed in the laboratory when $NaVO_3$ was added to MEA, H_2O, O_2, and CO_2.[57] Alternate construction materials are also under consideration and a recent study estimated a corrosion rate of 6.8×10^{-4} mm/year for aluminum nickel coating on carbon steel in 5 M MEA at 80 °C which is in the range of less than 5 μm/year and 0−1.1 mm/year for stainless steel measured at a number of pilot plants.[63,71] Consideration of other materials such as polymer linings may also be useful.

Evidently, as we progress toward commercial scale PCC, the management and control of corrosion will become a very significant consideration. Corrosion inhibitors have traditionally been used to minimize corrosion, but alternative nonmetallic inhibitors and construction or packing materials may be more effective for managing corrosion in PCC plants. Online monitoring of corrosion by using corrosometers[63] and by measurement of dissolved metals may be useful in commercial scale PCC.[43] However, the interdependence of corrosion and oxidative degradation must be understood before acceptable corrosion rates for aqueous amine based PCC can be determined.

3.4. SO_x. The flue gas in Australian coal-fired power station typically contains 100−600 ppm SO_2[51] and trace levels of SO_3.[64] Unlike most developed countries, Australian power stations are not required to remove SO_x from flue gas.[51] As SO_2 is very water-soluble, it rapidly oxidizes to sulfate in the presence of dissolved oxygen.[64,72] Sulfate is a much stronger acid than CO_2 and forms a heat stable salt (HSS) with amines such as MEA, reducing the CO_2 absorption capacity of the PCC solvent.[73]

A number of studies have been reported on the effect of SO_2 on MEA based PCC in laboratory scale experiments.[53,72,74] It was found that SO_2 in simulated flue gas accelerates oxidative degradation[53,74] and corrosion.[72] The latter may further accelerate oxidative degradation by increasing the concentrations of dissolved transition metals. Interestingly, the use of sulfur dioxide and its oxidation product, sulfite, has been considered in other studies for inhibition of the oxidative degradation of MEA by preferentially reacting with dissolved oxygen.[75,76]

It has been found that sulfur dioxide from flue gas (post FGD, flue gas desulfurization) was almost completely oxidized to sulfate and in the working solvent of the CASTOR pilot plant located at the Esbjerg coal-fired power station in Denmark.[23] This is also of particular concern for Victoria's brown coal-fired power stations where SO_x are not removed from the flue gas. At the pilot plant operated by CSIRO at Loy Yang Power (Australia), typical CO_2 and SO_2 concentrations of the flue gas are 10−11% and 120−200 ppm, respectively.[77] The worst case scenario of 1:2 conversion of SO_2 to the MEA-sulfate salt and 90% CO_2 capture equates to a consumption rate of 2−4 kg MEA/t CO_2 captured. This is greater than the total MEA consumption rate (1.4 kg MEA/t CO_2 captured) measured at a pilot plant at a black coal power station in Esbjerg, Denmark which has approximately 6 ppm SO_2 in the flue gas.[23] Hence, many PCC pilot plants use caustic scrubbers to ensure deep removal of SO_x to less than 10 ppm, even when FGD units are operated.[22,24,78]

3.5. Solvent Reclamation. A number of processes have been used in the natural gas sweetening industry to manage corrosion and solvent purity by separating heat stable salts and other degradation products from MEA (and other amine solvents) including distillation, electrodialysis, ion exchange or activated carbon filters.[7] These purification techniques are described in detail by Kohl and Nielsen[7] and typically treat a slipstream (commonly 10−20%) of lean solvent of gas sweetening plants. Mechanical and activated carbon filters were installed in the Niederaussem and Esbjerg pilot plants[23,24] and a thermal reclaimer is operated at the PCC facility at Trona, California.[43]

Distillation (commonly referred to as thermal reclamation) is only appropriate for MEA and other amines that are sufficiently volatile and stable at the temperatures required to distill the amine under vacuum, atmospheric, or desorber pressure.[7] Distillation removes suspended solids (such as residual fly ash), dissolved inorganics (such as dissolved metals from corrosion for fly ash) from the solvent. Addition of a strong base (commonly NaOH or Na_2CO_3) liberates the amine from heat stable salts, enabling the amine to distill with steam and return to the working solvent. Thermal reclamation exposes the amine solvent to higher temperatures and, hence, exacerbates solvent degradation and carries an energy penalty which is particularly significant for PCC where energy efficiency is of paramount importance.

In contrast, the use of activated carbon, electrodialysis and ion exchange techniques do not require high temperatures and, thus, reduces the possibility of severe MEA degradation.[7] Activated carbon filters are used to remove high molecular weight degradation products and reduce foaming in natural gas sweetening plants,[7] possibly by removing condensed hydrocarbons from the amine solvent. Electrodialysis and ion exchange have also been developed for natural gas sweetening and are typically combined with filtration to remove both suspended solids and charged molecules, such as sulfate, organic acid, and dissolved transition metals.[7]

The establishment of an effective solvent regeneration will therefore be beneficial in reducing the corrosivity of the solvent and solvent makeup during PCC by (a) avoiding accumulation of heat stable salts, and (b) minimizing the catalytic effect of transition metals on the degradation of MEA. As both heat stable salts and catalytic transition metals are charged at alkaline pH, electrodialysis and ion exchange may be the most effective solvent reclaiming techniques to be considered for operation of commercial scale PCC. However, solvent reclamation is likely to produce liquid or solid waste streams which must also be appropriately managed.

4. ENVIRONMENTAL MANAGEMENT

In its current state of development and operation, the net effect achieved by PCC of CO_2 with MEA is the substitution of the enormous anthropogenic CO_2 emissions of coal-fired power stations with low level emissions of ammonia and volatile organic compounds (VOCs), as well as aqueous and solid waste streams. However, to ensure that a commercial scale PCC has a net positive environmental impact, it is highly essential to give due consideration to the range and magnitude of byproduct that may result from the operation of such a process prior to its commencement. Preliminary environmental assessments of PCC conducted to date has suggested that human and environmental impacts will be mild,[35] but fresh water ecotoxicity is expected to increase.[36,37] These studies have considered both aqueous and gaseous emissions from direct and fugitive sources.[35] Gaseous emissions have been studied in the laboratory[58] and are also often monitored at pilot PCC plants.[23,24,51] However, wastewater or solid wastes from PCC is not commonly reported during pilot plant trials.[23,24] A fairly recent environmental concern is the detection of potentially carcinogenic nitrosamines in lean solvent from a PCC facility in Trona, California.[43] This has consequently initiated research into the formation and fate of nitrosamines and nitramines during PCC of CO_2.[36,39,40,51]

4.1. Nitrosamines and Nitramines. Nitrosamines and nitramines can be formed when organic amines and nitrosating agents (such as nitrate and nitrite)[79−81] are present in amine absorption solvent used for PCC. Nitrosamines have been detected in laboratory experiments[82] and in lean MEA solvent from a PCC plant at coal-fired power station in Trona, California,[43] while nitramines have been detected in MEA photochemistry experiments.[83] Many nitrosamines are carcinogenic[84] and commonly found in the environment,[84] metal-working fluids,[84−86] chlorinated and chloraminated water,[84,87,88] cosmetics,[84,89−91] some cooked or smoked foods,[84] and tobacco products.[84]

While nitrosamines are not formed from primary amines such as MEA, secondary and tertiary amines such as diethanolamine and triethanolamine, usually present as impurities in industrial grade MEA, are known to form nitrosamines.[79,80,92] Recent studies have investigated disproportionation reactions at 140 and 180 °C which may be another source of secondary and tertiary amines in MEA solvent.[82,93]

Typically, Australian coal-fired power station flue gas contains 100−300 ppm of NO_x[3,77] present primarily as nitric oxide (NO) with trace levels of nitrogen dioxide (NO_2) and nitrous oxide (N_2O).[64,77] Many coal-fired power stations use selective catalytic reduction (SCR) or selective noncatalytic reduction (SNCR) to reduce NO_x emissions and satisfy regulatory requirements.[64] Nitrosation is of particular concern in Australia where NO_x is not generally removed from coal-fired power station flue gas.[51,77]

In the atmosphere, NO is rapidly oxidized to NO_2,[94] but interestingly online FT-IR data from CSIRO's PCC pilot plant at Loy Yang Power in Victoria, Australia indicates that NO is the primary NO_x species entering the absorber column from the flue gas.[77] While NO has low water solubility, NO_2 is highly water-soluble[94] and is expected to dissolve in the aqueous amine solvent and oxidize to nitrite and nitrate. Make-up water and water used to dilute amine solvents for PCC is another source of dissolved nitrate and nitrite which can react with organic amines to form nitrosamines and nitramines.

A number of mechanisms have been proposed for the formation of nitramines and nitrosamines from nitrate, nitrite, and amines in neutral and acidic conditions.[79,80,92] More recently, Sun et al.[81] discussed the role of CO_2 as a catalyst for nitrosation and demonstrated that CO_2 can react directly with NO_2^- to form potent nitrosating agents. Carbonyl compounds (MEA oxidative degradation products) are also known to catalyze nitrosation of amines.[81] This may have important implications for PCC where alkaline aqueous amine solvents containing nitrite, nitrate and organic acids are in contact with an acidic flue gas containing CO_2 and NO_x.

Amines are also likely to be present along with NO and other NO_x species in the vapor phase during CO_2 absorption and in atmospheric emissions from PCC plants.[22,51] Acidic gases such as residual CO_2 and NO_x may render the vapor phase acidic, facilitating nitrosation. Trace levels of amines are also known to be emitted to the atmosphere, and both nitramines and nitrosamines have been detected in photochemical gas phase experiments.[83,95] Hence, nitrosamines and nitramines may be formed either in the vapor phase during PCC or within PCC atmospheric emissions.[83]

While nitrosation is unlikely to contribute significantly to solvent consumption, formation and release of carcinogenic nitrosamines to air and water may have serious human and environmental impacts. Further work is therefore necessary to establish the amounts of nitrosamines and nitramines that may be formed and released in wastewater or atmosphere. Although nitrosamines are unstable in UV light, their atmospheric impact and fate is poorly understood.[36] The influence of temperature, particulate material, and other compounds associated with coal-fired power station flue gas also need to be investigated.

Importantly, no reliable analytical method has been published for the determination of nitrosamines in aqueous amine solvent or vapor. Many methods and reviews have been published for analysis of nitrosamines in aqueous samples,[96−100] but are unlikely to be directly applicable to the analysis of nitrosamines in aqueous MEA or other amine solvents. In general, published methods involve extraction (usually solid phase extraction, SPE), derivatization and analysis by gas or liquid chromatography (GC or HPLC) but innovative techniques such as headspace SPME-GC/MS (solid phase microextraction−gas chromatography mass spectrometry) have also been useful.[99] However, care must be taken to prevent nitrosation or destruction of nitrosamines during sample storage and handling. A number of studies attempted to overcome this problem by adding ammonium sulfamate to samples[84] to react with residual NO_x. Due to its tendency to degrade in light, samples and extracts should be protected from light to minimize UV induced nitrosamine degradation.

4.2. Atmospheric Emissions. The assessment of the impacts of MEA and diethylamine emissions from a 1 Mt CO_2/year PCC plant in Norway on inhalation air quality, drinking water and deposition to aquatic ecosystems indicated an increased toxicity to aquatic ecosystems.[36] This observation is consistent with the estimates of the environmental impact of PCC of CO_2 from a natural gas fired power station.[37] A 12 t/year maximum tolerable emission of MEA was estimated, which is in the range of 10−30 t/year currently reported in literature.[36] Karl et al.[36] noted that their model assumed zero initial concentrations of carcinogenic nitramines and nitrosamines and a single source (PCC plant). Hence, actual human and environmental exposures are likely to be higher than estimated.[36]

VOC emissions to the atmosphere have also been investigated at both laboratory[58] and pilot scale.[23,24] Ammonia and MEA are the most commonly reported emissions.[23,24,58] Acetaldehyde and acetone have also been reported in pilot plant emissions,[24] while diethylamine, 2-butanol and methylactate have been detected in laboratory scale trials.[58] Laboratory trials indicate that CO_2, NO_x and SO_x concentrations, as well as temperature influenced the emissions volatile organic substances from aqueous MEA.[58] Importantly, photochemical smog chamber data indicate nitramines, acetamide and formamide are photochemical products of MEA and diethylamine also forms nitrosamines.[83] Recent studies and reviews have contributed to the understanding of the atmospheric fate of amines.[39,40,82]

4.3. Solid and Aqueous Wastes. The potential sources of aqueous wastes from PCC include water scrubbing of the lean flue gas to remove volatile organics such as aldehydes and amine solvent, spent solvent, condensate from the CO_2 product gas and incidental spills.[101] Solvent reclamation technologies also produce aqueous and solid waste streams from spent solvent, solvent impurities and mechanical or carbon filters.[101] An initial study indicated that anaerobic and aerobic biological treatments are feasible for treating wastewater from a PCC pilot plant, but an acidic source of carbon is needed to moderate the pH and increase the carbon to nitrogen ratio.[101] However, biological treatment was deemed inappropriate for aqueous waste from a Mexican natural gas sweetening facility containing diethanolamine (DEA).[101] Other options such as coincineration to reduce NO_x emissions have also been identified.[101] However, the characterization of solid and aqueous waste streams from current pilot plant programs is important to enable the design of safe handling, treatment and disposal options for aqueous and solid waste streams for commercial scale PCC of CO_2 from coal-fired power stations.

5. CONCLUSIONS AND FURTHER WORK

Substantial advances have been made in understanding the formation and fate of MEA degradation products at the laboratory scale and current pilot scale PCC programs have provided an excellent opportunity for validating this data.[24,41−43] The need to monitor and report gaseous, liquid and solid wastes has been highlighted in this review as a way of maximizing the value of pilot scale programs. This will provide the context for research into atmospheric chemistry of PCC emissions and reliable estimates of commercial scale PCC human and environmental impacts.

Oxidative degradation and solvent evaporation are considered the major sources of emissions to air[22,24,51] and have attracted a lot of interest.[23,37,42,52,53,58] However, characterization and treatment of wastewater generated from water scrubbing of lean flue gas at the exit of the absorber column, spent solvent, waste from solvent regeneration and incidental spills[101] is necessary. An initial study has indicated that biological treatments are viable,[101] but the potential environmental impact of wastewater from PCC has received very little attention.

Formation of nitrosamines and nitramines in both liquid and vapor phases of the PCC plant have the potential to significantly impact human and environmental health.[84] Elucidation of the mechanisms and rates of formation of nitrosamines and nitramines from NO_x and amine solvents both during PCC and in the atmosphere is of upmost importance to ensure human and environmental impacts of commercial scale PCC are understood and minimized. Reliable analytical methods are needed to measure the concentrations of nitrosamines at trace levels in amine solvents. Reliable determination of the amount of nitrosamines emitted to atmosphere and in wastewater is also necessary to enable the human and environmental impact of commercial scale PCC to be estimated.

The ability of transition metals to catalyze oxidative degradation may also have significant implications for operation and construction of commercial scale PCC plants. Measurement of the corrosion rates of 314 stainless steel at the pilot scale has been deemed acceptable for structural integrity. However, the concentrations of transition metals associated with corrosion and fly ash accumulated in solvent from residual fly ash or corrosion has not been reported at the pilot plant scale. A number of oxidation inhibitors have been investigated but the improvement of the fly ash removal during flue gas pretreatment may be more beneficial or alternatively the evaluation of construction and high surface area packing materials may be necessary. These are important considerations for progressing PCC toward commercial scale.

To improve the operation and maintenance of PCC plants, it may be helpful to monitor solvent degradation or solvent condition at- or online. Ammonia emissions have been used successfully to follow oxidative degradation at the laboratory scale[27,28,60] and many pilot plants are equipped to monitor ammonia emissions.[23,24,51] However, other factors such as dissolved metals, viscosity or color may be more important indicators of solvent condition. Indeed, the effects of contaminants (such as other amines, nitrite, nitrate, and dissolved metals) present in industrial grade MEA and water have not been investigated to date. Validating laboratory solvent degradation data at the pilot plant scale is an important step toward predicting the primary pathways of solvent degradation in commercial scale PCC and developing at- or online monitoring technology.

Solvent reclamation is an integral part of the natural gas sweetening industry[7] but has received little attention during the development of aqueous amine absorption for PCC. A number of technologies have been developed and used in the natural gas sweetening industry[7] and may be suitable for PCC. Adapting and developing technologies to separate degradation products (particularly charged sulfate, organic acids, and dissolved metals) from solvent may reduce corrosion, solvent degradation, and waste solvent, leading to reduced associated operating costs and human and environmental impacts of commercial scale PCC. However, solvent reclamation also generates aqueous or solid waste streams and appropriate methods of treating, reusing and disposing of these wastes need to be investigated.

Current PCC pilot plant programs provide excellent opportunities for validation of laboratory simulations of solvent degradation and volatile emissions. This is also an opportunity to develop and validate solvent reclamation and solvent monitoring technology for PCC. Extended waste monitoring and management practices which include liquid and solid wastes at the pilot scale is also very important and necessary. This should enable better solvent management practices and ultimately ensure that PCC of CO_2 from coal-fired power stations has a net positive human and environmental benefit.

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Notes

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A. ADDENDUM

This addendum reviews literature that became available following the submission of the preceding publication to *Environmental Science and Technology*. This thesis focuses on the degradation of MEA, and for this reason, most of the literature mentioned in this section focusses directly on the degradation of MEA.

A.1 Review of peer-reviewed literature since 2012

Recent International Energy Agency publications continue to argue that CCS (carbon capture and storage) development needs to be accelerated if it is to assist in maintaining atmospheric CO_2 concentrations below 450 ppm and suggest that financial, social and political barriers to CCS are more serious than technological barriers (International Energy Agency, 2012, 2013a, b). Along with other recent reviews, an IEA technology roadmap report identified the need for strategies to manage amine degradation and corrosion during PCC (Boot-Handford et al., 2014; International Energy Agency, 2013a).

A.1.1 Degradation of MEA at laboratory scale

Comprehensive reviews of the reactions and pathways of a range of common aqueous amine absorbents have been published recently (Gouedard et al., 2012; Vega et al., 2014). Although the range of aqueous amines used in degradation experiments has expanded in recent years, MEA remains the most extensively studied aqueous amine (Gouedard et al., 2012; Vega et al., 2014). These reviews also highlight parallels between the degradation of MEA and the degradation of other aqueous alkanolamines (Gouedard et al., 2012; Vega et al., 2014). These parallels are important because they suggest that observations of MEA degradation during pilot scale PCC will also be of value for understanding of the degradation of other alkanolamines during PCC.

Recent laboratory-scale experiments investigating the degradation of MEA have considered the influences of reaction apparatus on degradation rates and products (Vevelstad et al., 2013a; Vevelstad et al., 2013b; Vevelstad et al., 2014; Voice and Rochelle, 2013); differences between laboratory-scale degradation and degradation during pilot scale PCC (da Silva et al., 2012; Léonard et al., 2014a; Vevelstad et al., 2013c; Voice and Rochelle, 2013); the effect of organic anions, SO_x and NO_x on degradation rates and products (Aronu et al., 2014; Huang et al., 2013; Sun et al., 2014; Zhou et al., 2012); oxidation inhibitors (Voice and Rochelle, 2014); and the effects of fly ash and metals on degradation rates and products (Chandan et al., 2014; da Silva et al., 2012; Léonard et al., 2014b; Schallert et al., 2013). In general, these studies provide confirmation of the reaction pathways described in the main body of this chapter. More detail on these developments are given in the introductions to chapters 5 and 7.

A.1.2 Progress towards understanding MEA degradation at pilot, demonstration and commercial scales

Since 2012, a number of important pilot-scale amine degradation studies have become available. Moser et al (2011) published more details about the change in concentrations of organic anions, inorganic anions, cations and metals during a pilot plant campaign at Niederaussem. A second pilot-scale plant used for PCC of CO_2 from incinerator flue gas investigated the accumulation of HSS and measured the contributions of organic anions, sulfate and nitrate (Aouini et al., 2014). This pilot plant was constructed with alternative, non-metal materials (glass columns and ceramic column packing) and the sulfate concentrations were predicted to exceed the organic acid concentrations after more than 6000 h of operation (Aouini et al., 2014). This could indicate that the glass column and ceramic column packing were an effective corrosion mitigation strategy. However, the accumulation of HSS (formate, choride, NO_x and SO_x) during a third pilot-scale campaign of PCC from coal combustion flue gas also showed higher concentrations of sulfate than organic acids, although the pilot plant was operated for less than 200 h (Thompson et al., 2014). The further implications of these pilot plant results are discussed in detail in chapters 5 and 7.

The construction of a PCC facility at Mongstad, Norway, has initiated a significant body of research into the potential human health and environmental impacts (da Silva and Booth, 2013; de Koeijer et al., 2013). These studies have concluded that the emissions from PCC can be managed responsibly and recommended extensive environmental monitoring of early large scale PCC installations (da Silva and Booth, 2013). One related issue that has been discovered during recent pilot plant operations is the emission of aerosols from CO_2 absorber trains (Khakharia et al., 2013; Mertens et al., 2014a; Mertens et al., 2014b; Sharma and Azzi, 2014). A detailed discussion of aerosol formation and control is beyond the scope of this thesis but this issue does clearly highlight the (a) value of pilot scale PCC investigations and (b) the importance of careful consideration of the impact of flue gas impurities (including particulates) on the PCC process.

A.1.3 Other aspects of amine management

The interactions between aqueous amines, corrosion and fly ash have been considered in laboratory and/or pilot scale experiments since 2012. Unlike research into corrosion, research into the interactions between aqueous amines and fly ash is in the very early stages. The effects of MEA and organic anions on the metals and cations leached from fly ash samples has been investigated (Schallert et al., 2013). Two other studies demonstrated that MEA degradation was accelerated in the presence of fly ash from a variety of coals (Chandan et al., 2014; da Silva et al., 2012). This acceleration has largely been attributed to leaching of iron, which is known to catalyse oxidative degradation of MEA (Chandan et al., 2014; da Silva et al., 2012).

Since 2012, corrosion studies have been conducted at both laboratory and pilot scales. The key differences between separation of CO_2 from flue gases (i.e. PCC) and natural gas sweetening have been identified and discussed by Kittel et al. (2012). The comparatively high lean CO_2 loadings used to minimise the energy penalty of PCC, the presence of oxygen in flue gases and the choice of aqueous amine were identified as critical factors determining the corrosivity of amine absorbents during PCC (Kittel et al., 2012). The corrosion of metal coupons has been investigated during a pilot scale PCC campaign, demonstrating that the corrosion rates of 316 stainless steel were acceptable at all locations (Cousins et al., 2013). Other laboratory based corrosion studies have investigated the effects of flue gas impurities (including oxygen, chloride, NO_x and SO_x), organic acids, temperatures, oxidation potential and CO_2 loading (Fytianos et al., 2014; Pearson et al., 2013; Wattanaphan et al., 2013; Xiang et al., 2014).

A.1.4 Measuring amine degradation

Observations of amine degradation at laboratory, pilot, demonstration and commercial scale, requires effective and reliable measurement methods and technologies. Two types of methods have been explored since 2012: (a) laboratory-based methods including chromatography; and (b) on- or at-line technologies and methods. The continuous monitoring of amine concentrations and CO_2 loading during PCC has been achieved by use of spectroscopic and physio-chemical parameters (Einbu et al., 2012; Richner and Puxty, 2012; van der Ham et al., 2014; van Eckeveld et al., 2014; Zhu et al., 2013). The introduction of chapter 3 considers these developments and their implications for on-line or at-line monitoring of amine degradation in more detail.

The use and challenges of laboratory-based chromatographic methods for measuring amine degradation products have been well summarised by Ge et al. (2014) and the need for reliable methods has been identified by NIST (Espinal et al., 2013). Recently, HPLC/MS has been described as a more sensitive method than GC/MS (da Silva et al., 2012) and the validation of a HPLC/MS method has been described (Cuzuel et al., 2014). Alternative methods including proton transfer reaction mass spectrometry (PTR-MS) (Ge et al., 2014) and solid-phase microextraction with GC/MS (SPME-GC/MS) (Rey et al., 2013) have also been described recently. These developments and the challenges of GC/MS analysis are discussed in detail in the introduction of chapter 6.

A.1.5 Theoretical basis of heat-stable salts quantification methods

Interestingly, some questions regarding the theoretical basis of heat stable salts (HSS) quantification methods have arisen (Vevelstad et al 2013a). The basic principles underlying the HSS quantification method are briefly described in the introduction to chapter 4 and a HSS quantification method is described in section 2.4 (page 36). The four steps of this HSS quantification method are: (i) the addition of a molar excess of a strong cation exchange resin to a dilute amine solution; (ii) use of heat and stirring to increase the rate of cation adsorption onto the cation exchange resin; (iii) separation of the resin and the aqueous solution; (iv) acid-base titration of the acidic anions remaining in the aqueous solution.

The strong cation exchange resin (SCX, sulfonated styrene-divinylbenzene copolymer) used in HSS determinations are also used extensively in industrial, biochemical and industrial processes for purification and characterisation (Wheaton and Lefevre, 2000). Common applications include: ion exchange chromatography (i.e. ion chromatography); ion exchange solid phase extraction (i.e. the cation exchange SPE process described in chapter 6); and water purification in laboratories and commercial boilers. The theoretical basis of HSS quantification is also analogous to the theoretical basis of ion exchange amine reclamation procedures (Dumee et al. 2012).

The first step of HSS quantification (the addition of a molar excess of a SCX resin to a dilute solution of MEA) involves (a) acidification of the MEA solution; and (b) the adsorption of $MEAH^+$ to the resin. By definition, HSS are stronger acids than aqueous CO_2 species such as carbonic acid. For this reason, HSS form stronger ionic (or covalent) associations with weak bases such as MEA. Two model equations are shown below for sulfate (equation 1) and a generic organic acid (equation 2). In both reactions, cationic $MEAH^+$ and an anionic acid (HSS) combine to form a neutral species. Importantly, equations imply that removing $MEAH^+$ from the solution will dissociate both ionic and covalently bonded HSS by reversing reactions 1 and 2.

$2MEAH^+ + SO_4^{2-} \leftrightarrow [MEAH]_2SO_4$ (1)

$MEAH^+ + RCOO^- \leftrightarrow RCO\text{-}MEA + H_2O$; RCO-MEA is an amide (2)

A molar excess of the cation exchange resin added to the aqueous MEA ensures that reaction 3 proceeds in the forward direction, thereby reducing the pH and acidifying MEA. The exchange of protons for $MEAH^+$ (i.e. reaction 3) results in the net reversal of reactions 1 and 2. The rates of reactions 1-4 are increased by heating and rapidly stirring the resin and dilute MEA solution for up to 1 h.

The resin (with adsorbed $MEAH^+$) is then separated from the remaining aqueous solution by filtration. Unlike MEA, the negatively charged HSS anions (e.g. sulfate and organic acids) do not bond to the strong cation exchange resin. An important distinction between reactions 3 and 4 is that an acid is produced in reaction 4 (i.e. exchange of MEA from a HSS to the resin) but no acidic protons are produced in reaction 3 (i.e. adsorption of a free MEA molecule onto the resin). This means that after cation exchange, the acid form of the HSS anions are present in the aqueous solution and can be quantified by acid-base titration (the third and final step of HSS quantification) without interferences from MEA.

$MEA + Resin\text{-}SO_3\text{-}H \leftrightarrow Resin\text{-}SO_3\text{-}MEAH^+$ (3)

$(MEAH)_2SO_4 + 2Resin\text{-}SO_3H \leftrightarrow H_2SO_4 + 2Resin\text{-}SO_3(MEAH)$ (4)

Preparation and/or regeneration of the cation exchange resin is an integral step of all ion exchange procedures (Wheaton and Lefevre 2000). The cation exchange resins are typically supplied in the sodium form (i.e. the counter ion on the sulfonic acid groups is sodium as shown on the reactant side of reaction 5). The sodium counter ions are exchanged to a weaker cation to enable the resin to be used to remove cations (e.g. $MEAH^+$) from the solution. Protons are a commonly used weak cation (Wheaton and Lefevre 2000) and the exchange of sodium for protons is achieved by heating the resin in the presence of a concentrated strong acid (e.g. hydrochloric acid). Excess HCl and NaCl can be removed by rinsing the resin with copious volumes of deionised water. To regenerate the resin after use, the $MEAH^+$ bound onto the cation exchange resin are exchanged with protons using the same process.

$HCl + Resin\text{-}SO_3Na \leftrightarrow NaCl + Resin\text{-}SO_3H$ (5)

The use of a strong cation exchange (SCX) resin to (a) acidify a dilute MEA solution and (b) adsorb cations enables the quantification of acidic anions by acid-base titration. The key advantage of this method is that it provides a non-specific measurement of HSS anions without the use of sophisticated equipment. However, HSS determinations by cation exchange and acid-base titration are unable to distinguish between different types (i.e. organic or inorganic) or sources (i.e. oxidative amine degradation or flue gas contaminants) of HSS anions.

A.2 Conclusion

Overall, the research since 2012 has validated the recommendations presented in the main text of this chapter. Some important progress has been made towards: (i) observations of amine degradation and emissions at pilot scale; (ii) measuring interactions between aqueous amines, metals and fly ash at laboratory scale; (iii) the construction of PCC pilot plants using non-metallic materials; (iv) the development of on- and/or at-line amine monitoring methods; and (v) the evaluation of amine reclamation strategies. In addition, the need for validation of analytical methods for identification and quantification of amine degradation products (including, but not limited to nitrosated amines) in amine absorbents has become clear.

Chapter 3: MEA quantification

Quantification of aqueous monoethanolamine concentration by gas chromatography for post-combustion capture of CO_2

This chapter demonstrates that the MEA concentrations measured by GC-FID (gas chromatography with flame ionisation detection) and by acid-base titration are equivalent and that both of these methods were suitable for measuring MEA concentrations in the MEA absorbent sampled from CSIRO's pilot plant at Loy Yang. This chapter is comprised of a paper that has been published by *Industrial and Engineering Chemistry Research* in 2014. The full reference for this paper is:

Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Chaffee, A., Meuleman, E., 2014. Quantification of Aqueous Monoethanolamine Concentration by Gas Chromatography for Postcombustion Capture of CO_2. Industrial & Engineering Chemistry Research 53, 4805-4811

The MEA concentrations measured by the GC-FID method described in this paper are used in the following chapters. Furthermore, the lessons learned in the preparation of this chapter were valuable for the development of the GC/MS method presented in chapter 6.

Declaration for Thesis Chapter 3

Declaration by candidate

In the case of Chapter 3, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Defined the aims and scope of the manuscript, conducted all the laboratory work, wrote the initial draft of the paper and coordinated feedback and comments from all authors.	80

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
T. Vincent Verheyen	Provided valuable advice on the use and interpretation of data presented in this manuscript. Provided valuable advice on the structure, content and presentation of the manuscript.	N/A
Samuel B. Adeloju	Valuable advice on the structure, content and presentation of the manuscript. Co-ordinated submission and revision of the article	N/A
Erik Meuleman	Provided the sample set and associated pilot plant operation data. Originally identified the need for the development of techniques for monitoring amine degradation. Provided valuable comments on the final drafts.	N/A
Alan L. Chaffee	Valuable input into final drafts	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature	A Reynolds	**Date** 31-Mar-2015
Main Supervisor's Signature		**Date** 31/3/15

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

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Quantification of Aqueous Monoethanolamine Concentration by Gas Chromatography for Postcombustion Capture of CO_2

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ABSTRACT: The availability of reliable analytical methods for measuring amine concentrations is necessary for optimum operation of aqueous amine CO_2 separation systems being employed for postcombustion capture (PCC) of CO_2. A GC-FID (gas chromatography with flame ionization detection) method is described for the reliable quantification of 30% (w/w) monoethanolamine (MEA) in severely degraded solvent samples. The observation of intermittent splitting of the MEA peak was a major concern with this approach. The use of a wide-bore column led to improved MEA peak resolution and peak shape. The reliability and robustness of the GC-FID method were assessed by analyzing degraded 30% (w/w) MEA solvent samples from CSIRO's pilot plant at AGL's Loy Yang power station in Victoria, Australia. The results were compared with those obtained by titration and total organic carbon (TOC) measurements of the same samples. The MEA concentrations obtained by the GC-FID and titration methods were statistically similar. In contrast, the MEA concentrations calculated from TOC were consistently higher than those obtained by both GC-FID and titration.

■ INTRODUCTION

The aqueous amine gas separation technologies originally developed by the natural gas treating industry have provided the basis for the most mature technology for postcombustion capture (PCC) of CO_2 from flue gases of fossil-fuel-fired power stations.[1] Aqueous amine solvents are key components of these systems and considerable research effort is directed toward the development of novel solvents with lower energy requirements.[2] Maintaining consistent solvent concentrations is critical for minimizing energy use and managing corrosion.[3]

As PCC moves toward commercial deployment, reliable measurement of amine concentrations will be more challenging and more important than traditional applications of this technology because (a) economic and energy efficiency are critical,[2] (b) advanced solvents are often mixtures of amines,[2] and (c) solvent degradation is likely to be more severe due to higher CO_2 concentrations in lean solvents and exposure to flue gas.[4] Under these conditions, heat-stable salts (including sulfates from oxidation of SO_x in flue gas, organic acids from oxidative degradation, and other anions) are likely to accumulate in PCC solvents.[4,5] For these reasons, it is essential that the analytical techniques used to measure aqueous amine concentrations are rapid, reliable, not significantly influenced by solvent degradation products, and capable of measuring the concentrations of multiple amines.

Acid−base titration is an established analytical method for measuring aqueous amine concentrations, but it is susceptible to interferences from degradation products (particularly organic acids) and is generally unable to distinguish among different amine species.[6] Traditionally, color indicators such as methyl orange, methyl red, or bromophenol blue have been used to detect the titration end point.[7−9] More advanced titration methods[6,10] use potentiometric titrations to determine the equivalence points. Cummings et al.[11] demonstrated that monitoring conductance during a titration further reduces interferences from heat-stable salts because the equivalence points of organic acids can be distinguished from those of the target amine.

Since the 1960s, there has been considerable interest in using chromatography for measuring amine concentrations.[7,8,12,13] The earliest gas chromatography (GC) methods were hampered by reactive inlet systems, use of poor column materials, chemical reactivity, and difficulties in derivatizing amines in an aqueous matrix.[7,8,12,13] In recent times, the inlet systems and columns available for both gas and liquid chromatographic techniques have improved markedly. A significant advantage of chromatography is the ability to determine the concentrations of individual amine species in blended solvents. Ion chromatography has become a popular method of choice,[14,15] but both high-performance liquid chromatography (HPLC) and gas chromatography (GC) are also capable of providing rapid, robust, and reliable quantification of amines.

Other common elemental techniques, such as total organic carbon (TOC) and total nitrogen, are rapid and well-established, but they are susceptible to interferences because they cannot distinguish between elements in degradation products and the target amines. Attenuated-total-reflectance infrared (ATR-IR) spectroscopy combined with partial least-

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squares (PLS) regression has proven effective for rapid quantification of monoethanolamine (MEA) and CO_2 and classification of the condition of the solvent.[16,17] A distinct advantage of ATR-IR spectroscopy is its ability to be used in situ.[16,17] A combination of precise refractive index and density measurements has also been used to quantify MEA, methyl diethanolamine (MDEA), and CO_2 in water.[18] However, this method is not likely to be suitable for degraded solvents because of the complexity of physiochemical changes resulting from solvent degradation.[18]

In this study, we investigated the use of a GC-FID (gas chromatography with flame ionization detector) method for the reliable measurement of 15−45% (w/w) MEA concentrations in aqueous samples. The reliability of this GC-FID method and a TOC method was validated by using severely degraded 30% (w/w) MEA samples from CSIRO's postcombustion CO_2 capture (PCC) pilot plant at AGL's Loy Yang power station. These methods are also compared with acid−base titration, an industry standard method for measuring MEA concentration.

■ MATERIALS AND METHODS

Sample and Other Reagents. To assess the robustness of the GC-FID and TOC methods for aged solvent samples, seven samples of 30% (w/w) MEA solvent were obtained from a PCC pilot plant operated by CSIRO (Commonwealth Scientific and Industrial Research Organization, Australia). A batch of 30% (w/w) MEA solvent was used for 640 h during rich-split desorber modifications[19] and corrosion investigations[20] at a PCC pilot plant operated by CSIRO at Tarong, Queensland, Australia (Stanwell's 1400 MW black coal-fired power station). The solvent was stored for 18 months in a plastic intermediate bulk container (IBC) before being used in CSIRO's PCC pilot plant at Loy Yang, Victoria, Australia (AGL's 2210 MW brown coal-fired power station) for a further 500 h. The solvent samples used in this study were sampled periodically from the pilot plant at Loy Yang into high-density polypropylene bottles, immediately transferred to a laboratory, and stored at −20 °C in the dark. The samples are described in Table 1.

Table 1. Descriptions of the 30% (w/w) MEA Samples Obtained from CSIRO's Pilot Plant at Loy Yang

sample	date of sample	hours of operation at Loy Yang	tonnes of CO_2 captured at Loy Yang
1	2-Aug-2012	5	0.1
2	14-Aug-2012	57	1.2
3	21-Aug-2012	113	2.4
4	29-Aug-2012	189	3.8
5	4-Sep-2012	242	4.9
6	11-Sep-2012	309	6.0
7	18-Sep-2012	372	7.3

Titration. Approximately 1 g of sample was accurately weighed, diluted to approximately 50 mL, and acidified with 10 mL of 1 M HCl. Excess HCl was titrated against 0.5 M NaOH using a Mettler-Toledo T50A autotitrator with an automated beaker stand (Rondolino) and a combined glass pH electrode with a fixed ground-glass sleeve junction (DGi-115-SC). The MEA concentration was calculated from the number of moles of HCl consumed prior to titration. MEA concentrations are reported as averages of two concordant results.

Total Organic Carbon (TOC). Samples were diluted 1:100 by mass into 40 mL vials with fresh deionized water (18.2 MΩ/cm, Milli-Q Academic, Millipore) before both inorganic carbon (acid-purgeable CO_2) and total carbon (combustion method) were measured using a Shimadzu TOC-V analyzer. Injections of 50 μL were used for both total and inorganic carbon analyses. A further 1:10 dilution was conducted by the instrument for total carbon analysis. TOC was determined as the difference between total carbon and inorganic carbon. MEA concentrations were calculated from the TOC, assuming that MEA was the predominant form of organic carbon (i.e., organic carbon in compounds from oxidative degradation and carbamate polymerization were insignificant).

MEA (Chem Supply, >99% purity), total carbon (potassium hydrogen phthalate, Sigma-Aldrich, 99.95% purity), and inorganic carbon (sodium carbonate and sodium hydrogen carbonate, BDH Chemicals, >99% purity) standards were diluted with deionized water (18.2 MΩ/cm, Milli-Q Academic, Millipore) for TOC analyses. Before being weighed, potassium hydrogen phthalate and sodium hydrogen carbonate were dried at 105 °C overnight, and sodium carbonate was dried at 290 °C for 3 h and stored in a desiccator with silica gel.

Gas Chromatography with Flame Ionization Detection (GC-FID). Approximately 0.1 g of sample was accurately weighed into an amber silanized GC vial and made up to 1 g with deionized water (18.2 MΩ/cm, Milli-Q Academic, Millipore). Then, 10 μL of this 1:10 dilution was transferred to another amber silanized GC vial containing 990 μL of 0.1% ammonium hydroxide (BDH Chemicals, approximately 35% w/w) and 25 mg/L d_5-pyridine (internal standard, Cambridge Isotope Laboratories, 99.5% purity) in deionized water.

Standards were prepared from appropriate masses of MEA (Chem Supply, >99% purity) diluted with deionized water (18.2 MΩ/cm, Milli-Q Academic, Millipore) containing approximately 0.1% ammonium hydroxide (BDH Chemicals, Aristar, approximately 35% w/w) and 25 mg/L d_5-pyridine (Cambridge Isotope Laboratories, 99.5% purity).

MEA was quantified by GC-FID (CP3800 with CP8400 autosampler, Varian) using a 15-m, 0.53-mm i.d., thick-film (1.5-μm) 5% phenyl/95% dimethylsiloxane column from SGE (BP5, Melbourne, Victoria, Australia). Other GC-FID conditions for the final method were as follows: 0.3-μL injection, 260 °C injector temperature, 1177 injector, SGE focus liner, 1:10 split, 335 °C detector temperature, and electronic flow controller delivering 2.8 mL/min helium carrier gas with a 2.0 psi pressure pulse for 0.25 min after injection. The column oven program was 70 °C for 1 min, ramp to 100 °C at 10 °C/min, ramp to 320 °C at 20 °C/min, and hold for 3 min. MEA eluted at 2.4 min, and the total run time was 18 min but could be shortened if required.

Columns tested during development of the GC-FID method include 100% dimethylsiloxane (ZB-1, 60 m, 0.25-mm i.d., 1-μm film thickness; Phenomenex, Torrance, CA), 5% phenyl/95% dimethylsiloxane (CP-Sil 5CB, 15 m, 0.25-mm i.d., 0.25-μm film thickness; Agilent Technologies, Palo Alto, CA), 35% phenyl/65% dimethylsiloxane (HPX35, 30 m, 0.25-mm i.d., 0.25-μm film thickness; SGE, Melbourne, Victoria, Australia), 6% cyanopropylphenyl/94% dimethylsiloxane (CP-Select 624, 30 m, 0.25-mm i.d., 1.4-μm film thickness; Agilent Technologies, Palo Alto, CA) and polyethylene glycol (Sol−Gel Wax, 30 m, 0.25-mm i.d., 0.25-μm film thickness; SGE, Melbourne, Victoria, Australia).

Table 2. Width, Asymmetry, and Retention of MEA Dissolved in Water on Selected Columns

column phase	column dimensions[a]	mass of MEA injected onto the column[b] (ng)	width of MEA peak at half-height (s)	asymmetry factor[c]
100% polyethylene glycol	30 m, 0.25 mm, 0.25 μm	3	4.90	9.5
6% cyanopropylphenyl/94% dimethylsiloxane	30 m, 0.25 mm, 1.4 μm	15	1.89	11.1
35% phenyl/65% dimethylsiloxane	30 m, 0.25 mm, 0.25 μm	15	1.61	2.8
5% phenyl/95% dimethylsiloxane	15 m, 0.25 mm, 0.25 μm	7.5	0.78	1.3
100% dimethylsiloxane	60 m, 0.25 mm, 1 μm	4.5	2.76	1.3

[a] Length, internal diameter, film thickness. [b] Amount of MEA injected on the columns varied in an effort to produce a good-quality MEA peak. [c] Asymmetry factor calculated at 5% of the peak height.

■ RESULTS AND DISCUSSION

Troubleshooting the GC-FID Method. Established GC methods for measuring the concentrations of acidic polar organic compounds in aqueous matrixes are widely available in the peer-reviewed literature,[22−25] but very little information is available for the analysis of basic compounds in aqueous matrixes. In this study, the most appropriate column phases were selected by comparing the MEA peak shapes on five different column phases. The effects of variable pH and acidic contaminants in the samples were minimized by diluting samples in an alkaline and volatile buffer, ammonium hydroxide. However, the most important challenge was preventing the intermittent splitting of the MEA peak by use of a wide-bore column.

Strongly tailing peaks indicate severe interactions between the analyte and the chromatographic system. These peaks are difficult to integrate reliably and often lead to reduced analyte response.[22,23] The peak shapes of polar compounds such as amines are particularly sensitive to active sites in gas chromatographs (such as exposed silica and deposits in inlet liners or columns) and dipole−dipole or ionic interactions with the column phase.[21,22] The widths and asymmetry factors of the MEA peak on five different column phases are reported in Table 2. The mass of MEA injected onto each column and the column oven temperature program were varied to provide each column with a fair chance of producing a MEA peak with a good peak shape. All of the columns investigated were capable of separating MEA from the aqueous solvent. Strong hydrogen-bonding interactions between MEA and both of the polar column phases (100% polyethylene glycol and 6% cyanopropylphenyl/94% dimethylsiloxane) resulted in tailing peaks with high asymmetry factors. The nonpolar column phases produced MEA peaks with acceptable peak shapes and asymmetry factors close to unity. The 100% dimethylsiloxane and 5% phenyl/95% dimethylsiloxane column phases were chosen for further investigations.

Acidification of aqueous matrixes prior to the analysis of short-chain fatty acids is commonly used to prevent ionization and ensure reproducible recovery of the analytes.[22−25] In this study, all samples and standards were diluted 1:1000 in a volatile buffer (0.1% ammonium hydroxide) to convert MEA to its neutral form, ensure that the pH values of samples and standards were consistent, and shield MEA from acidic sites in the GC system. The increased MEA response in the presence of ammonium hydroxide is evident in Figure 1.

However, intermittent splitting of the MEA peak was observed on these nonpolar columns even though a good peak shape was consistently obtained for d_5-pyridine. Peak splitting during GC analysis of polar compounds in aqueous solvents is often attributed to partial ionization of the analyte or adsorption of the analyte onto active sites in the gas chromatograph.[22,23] In an effort to prevent intermittent splitting of the MEA peak, the impacts of injector liner (use of deactivated glass wool and cleanliness), injector temperature (180−280 °C), injection volume (0.2−1.5 μL), column phase, column-phase thickness (0.25 and 1 μm), column condition, concentration of MEA (60−6000 mg/L), concentration of ammonium hydroxide (0−0.1%), and injector split (splitless to 1:80) were investigated. Table 3 shows that the frequency of the MEA peak splitting was effected by the injector temperature, the design and cleanliness of the injector liner, and the concentration of ammonium hydroxide. Removing the front 20 cm of the column (where nonvolatile compounds are most likely to deposit) usually decreased the frequency of MEA peak splitting for a few injections. However, these changes did not stop the intermittent splitting of the MEA peak.

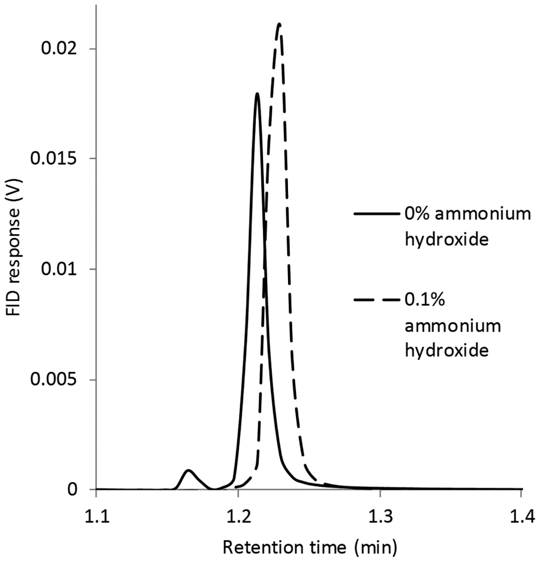

Figure 1. Effect of ammonium hydroxide on the retention and response of 300 mg/L MEA on a 5% phenyl/95% dimethylsiloxane column (CP-Sil 5CB 15 m, 0.25-mm i.d., 0.25-μm film thickness; Agilent Technologies, Palo Alto, CA).

Peak splitting was not observed during analyses of other compounds in the MEA solvent using gas chromatography−mass spectrometry (GC−MS) systems,[9,26,27] which operate at lower pressures to compensate for the vacuum at the column outlet. It was also observed that the MEA peak was less likely to split when a smaller volume was injected (Table 4) and more

Table 3. Effects of Injector Temperature, Injector Liner, and Column Condition on the Frequency of MEA Peak Splitting Using a 5% Phenyl/95% Dimethylsiloxane Column[a,b]

description	injector temperature (°C)	ammonium hydroxide concentration (%)	frequency of peak splitting	number of observations
standard conditions	260	0.1	0.37	24
	180	0.1	0.83	6
	260	0.1	0.67	6
	180	0	1.00	6
new injector liner (no glass wool)	180	0	0.67	6
front 20 cm of column removed	260	0	0.00	6
	180	0.1	1.00	6
front 20 cm of column removed	260	0.1	0.00	6
	260	0.1	0.33	3
front 20 cm of column removed	260	0.1	0.67	3
	260	0.1	1.00	4
injector liner cleaned[c]	260	0.1	0.67	6

[a] CP-Sil 5CB 15 m, 0.25-mm i.d., 0.25-μm film thickness; Agilent Technologies, Palo Alto, CA. [b] Analyses conducted over three consecutive days and presented in chronological order. [c] Injector liner immersed in 1:1 methanol/deionized water in an ultrasonic bath for 5 min, rinsed with 0.1% ammonium hydroxide, and dried.

Table 4. Effects of Injection Volume and Column Internal Diameter on the Frequency of MEA Peak Splitting

column dimensions[a]	injection volume (μL)	mass of MEA injected onto the column (ng)	frequency of peak splitting	number of observations
15 m, 0.25 mm, 0.25 μm	1	15	0.37	24
15 m, 0.25 mm, 0.25 μm	0.3	4.5	0.21	24
15 m, 0.53 mm, 1.5 μm	0.3	4.5−13.5	0	61

[a] Length, internal diameter, film thickness.

Table 5. Effect of Pressure Pulse on the Frequency of MEA Peak Splitting Using the Wide-Bore, Thick-Film 5% Phenyl/95% Dimethylsiloxane Column[a]

pressure pulse (psi)	frequency of peak splitting	number of observations
2	0.00	7
4	0.00	7
6	0.71	7
8	0.57	7

[a] 15 m, 0.53-mm i.d., 1.5 μm; SGE, Melbourne, Victoria, Australia.

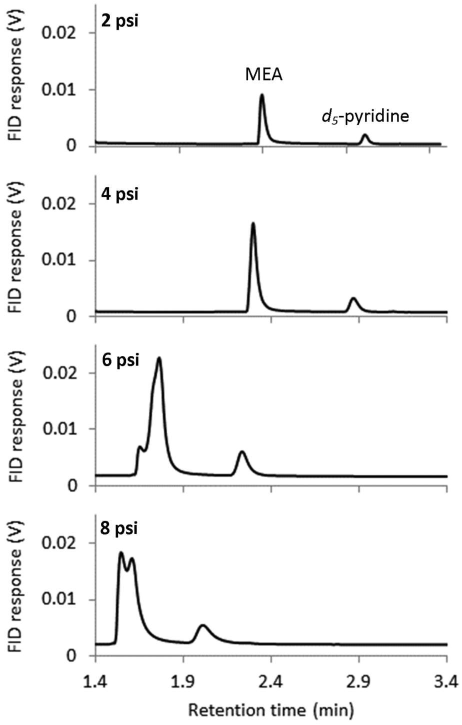

Figure 2. Effect of pressure pulse on the peak shape of 300 mg/L MEA using the wide-bore, thick-film 5% phenyl/95% dimethylsiloxane column (15 m, 0.53-mm i.d., 1.5 μm; SGE, Melbourne, Victoria, Australia).

likely to split when a pressure pulse was applied during injection. Table 4 also shows that MEA peak splitting was not observed during a batch of 61 GC-FID analyses of samples and standards using a wide-bore, thick-film 5% phenyl/95% dimethylsiloxane column (BP5, 15 m, 0.53-mm i.d., 1.5 μm; SGE, Melbourne, Victoria, Australia). The optimum flow rate (2.8 mL/min) for the wide-bore column required just 1.1 psi at the initial oven temperature, which is well below the 12.9 psi required to maintain a 1 mL/min helium flow in a standard 30-m, 0.25-mm-i.d. column.

The correlation between carrier-gas pressure and MEA peak splitting was tested in the wide-bore column system by applying pressure pulses of 2, 4, 6, and 8 psi for 0.25 min after injection. Table 5 shows that the frequency of splitting of the MEA peak was lower with a pressure pulse of 2 or 4 psi than with a pressure pulse of 6 or 8 psi. In all cases, the d_5-pyridine peak shape remained acceptable (see Figure 2 for typical chromatograms). The dependence of MEA peak splitting on the injection pressure suggests that peak splitting might be caused by MEA interacting with condensed water in the column. Figure 3 shows that, once the optimum pressure pulse was employed, both MEA standard and sample diluted with 0.1% ammonium hydroxide gave well-resolved chromatographic peaks when analyzed with the wide-bore, thick-film 5% phenyl/95% dimethylsiloxane column.

GC-FID and TOC Method Validation. Table 6 shows that both GC-FID and TOC methods exhibited linear response in their applicable analytical ranges [equivalent to 15−45% MEA (w/w)]. The detection limits were well below the required analytical ranges, and MEA recoveries for both methods were between 90% and 110%. The relative standard deviation of the area of the d_5-pyridine peak for the 15 GC-FID calibration analyses was 2.3%. These results indicate that both methods are suitable for measuring MEA concentrations in aqueous samples.

Comparison of the GC-FID and TOC Methods with the Titration Method. The susceptibility of acid−base titrations to interference from heat-stable salts (HSSs) has long been acknowledged, and although a detailed discussion of the HSS

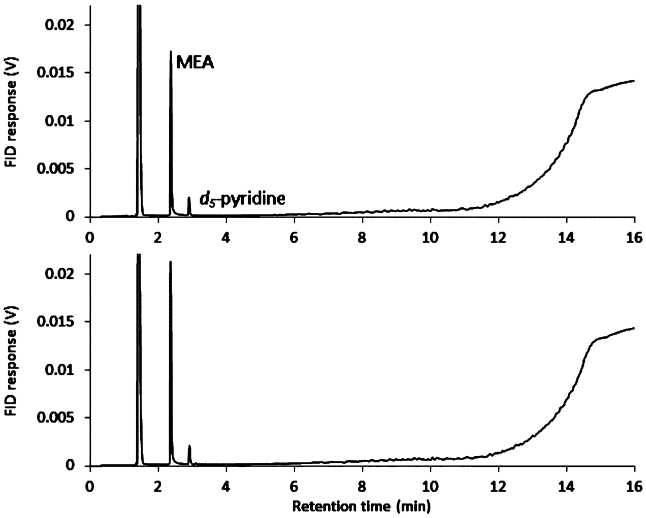

Figure 3. Typical chromatograms of a 300 mg/L MEA standard (top) and sample 7 (bottom) diluted in 0.1% ammonium hydroxide using the wide-bore, thick-film 5% phenyl/95% dimethylsiloxane column (15 m, 0.53-mm i.d., 1.5 μm; SGE).

Table 6. Summary of Method Validation Parameters for GC-FID and TOC

	applicable analytical range[a] (mg/L)	R^2	IDL[b] (mg/L)	recovery[c] (%)
GC-FID	150−450	0.991	10	104 ± 4
TOC	15−45	0.999	1.5	107 ± 4

[a]Concentration range measured at the instrument for samples containing 15−45% MEA (w/w). [b]Instrument detection limits (IDLs) calculated as the standard deviation of seven replicates multiplied by the Student's *t* value (99% confidence, one-tailed). [c]Recoveries calculated from samples fortified with MEA. The uncertainty is the mean deviation of three measurements.

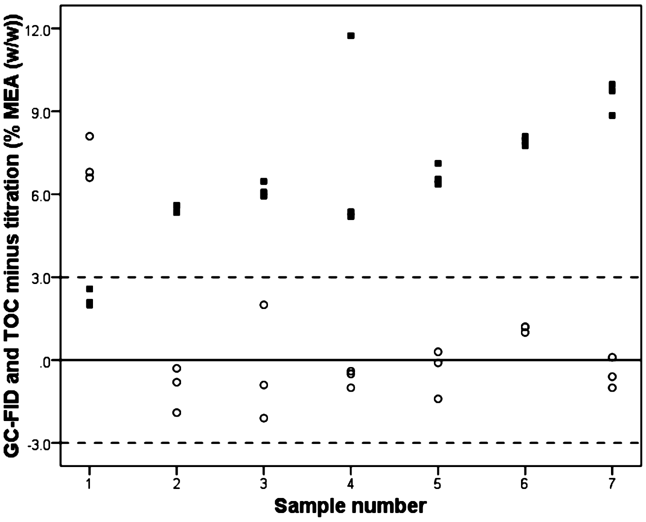

Figure 4. MEA concentrations measured by TOC (solid squares) and GC-FID (open circles) subtracted from the MEA concentrations measured by titration. Data points on the solid line are identical to the titration result, and data points within the broken lines differ from titration by less than 3% (w/w) MEA [10% error for a 30% (w/w) MEA solvent]. Samples were obtained over 500 operating hours and are numbered in order of age. The details for each sample are provided in Table 1.

concentrations in these samples or measurement methods is beyond the scope of this article, the potential of HSSs to interfere with acid−base titrations is an important consideration. The HSS concentrations of these samples (measured by acid−base titration after removal of cations by ion exchange and filtration) were all less than 2% (w/w, as MEA, data not shown). This limits the interference from HSSs to 2% (w/w, MEA), which is less than a 10% error in a 30% (w/w) MEA solvent. Despite the potential for interferences from HSSs, acid−base titrations are currently the industrial standard method for measuring MEA concentrations and have been used in a number of pilot-scale PCC campaigns.[19,28] For these reasons, we compared the MEA concentrations measured by both GC-FID and TOC methods with the MEA concentrations measured by acid−base titrations.

Figure 4 shows the GC-FID and TOC measurements subtracted from the MEA concentration measured by acid−base titration for each of the seven samples from CSIRO's pilot plant at AGL's Loy Yang power station. With the exception of sample 1, the titration and GC-FID measurements agreed to within 3% MEA (w/w). However, the MEA concentrations measured by TOC were all higher than the titration measurements, and the discrepancies were generally larger than 3% MEA (w/w).

Sample 1 was unique because the MEA concentrations measured by GC-FID were consistently higher than both the titration and TOC results. The TOC method does not distinguish between MEA and other organic species and, hence, provides a theoretical maximum MEA concentration. As the GC-FID measurement was higher than the TOC measurement, the former is most likely to have been erroneous for this sample. Sample 1 was taken shortly after the solvent was stored in a plastic container for 18 months. A plausible explanation for this erroneous MEA measurement is the presence of a volatile contaminant from previous use of the storage container that coeluted with MEA, had a relatively high FID response and a low TOC response and might have evaporated from the solvent by the PCC process. As a result, sample 1 was excluded from further analysis of GC-FID measurements.

The absolute discrepancies between GC-FID and titration measurements for samples 2−7 were less than 3% (w/w) MEA [i.e., 10% error for a 30% (w/w) MEA solvent]. The Student's *t* test (one-sample test, 95% confidence interval from −0.53 to 2.08, significance level of 0.230) confirmed that there was no significant difference or bias between the mean values obtained by of GC-FID and titration. The agreement of MEA concentrations measured by these two different methods suggests that both are appropriate for determining MEA concentrations of aged solvents within 10% error. A valuable advantage of the GC-FID method is that, with minor modifications of the column oven program, calibration with appropriate standards, and method validation, it is likely to be an appropriate method for measuring concentrations of individual species in mixed amine solvents.

The data in Table 7 and Figure 4 indicate that the MEA concentrations in samples 1−7 measured by TOC were all higher than the concentrations measured by titration despite good recovery of MEA from fortified samples (Table 6). The Student's *t* test confirmed that the means of the MEA concentrations calculated from TOC were significantly higher than those obtained by titration (one-sample test, 95% confidence interval of 5.4−7.6, significance level of <0.001).

Table 7. MEA Concentrations (%, w/w) of Seven Samples Measured by Titration, GC-FID, and TOC[a]

sample	titration	GC-FID	TOC
1	27.96 ± 0.04	35.2 ± 0.6	29.6 ± 0.2
2	31.3 ± 0.2	30.3 ± 0.6	36.8 ± 0.1
3	31.94 ± 0.04	31.6 ± 2	38.1 ± 0.2
4	27.90 ± 0.09	27.3 ± 0.2	35.3 ± 3
5	27.84 ± 0.06	27.4 ± 0.7	34.5 ± 0.3
6	29.64 ± 0.02	30.7 ± 0.09	37.5 ± 0.1
7	28.96 ± 0.05	28.5 ± 0.4	38.5 ± 0.4

[a] Concentrations presented as the averages of two (titration) or three (GC-FID and TOC) measurements ± mean deviation.

This bias is consistent with interferences from neutral and acidic MEA degradation products (such as organic acids from oxidative degradation and neutral compounds from carbamate polymerization[5]), which are included in TOC measurements but excluded from titration and GC-FID measurements. These results demonstrate that the interferences from organic carbon sources other than MEA are significant and that the TOC method is not suitable for measuring MEA concentrations in these aged solvents.

Figure 4 also shows that the discrepancies between the MEA concentrations obtained by the TOC and titration methods were measurable and increased during the PCC campaign. The primary source of organic carbon other than MEA in these solvent samples is the degradation of MEA. This suggests that the discrepancy between the TOC and MEA concentrations measured by GC-FID and titration (Table 7) might be a useful and easily measured indicator of MEA degradation.

■ CONCLUSIONS

A reliable GC-FID method has been developed for measuring MEA concentrations in aqueous solutions. This method has successfully overcome peak splitting and poor recovery issues with GC-FID, which are common problems for direct injection of aqueous alkaline samples. This GC-FID method is comparable in performance to the industry standard method (acid−base titration) for measuring MEA concentrations in 30% (w/w) MEA PCC solvent samples. This method could be easily modified to measure multiple amines in the mixed amine solvents that are currently under development.

In contrast, comparison of the GC-FID and titration results revealed a large discrepancy with the results obtained by TOC. The TOC method is not able to distinguish between different amine species in mixed amine solvents. However, TOC measurements might be useful for validating suspicious amine concentration measurements from other techniques or monitoring the accumulation of organic degradation products.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

ATR-IR = attenuated-total-reflectance infrared spectroscopy
GC-FID = gas chromatography with flame ionization detection
MEA = monoethanolamine
PCC = postcombustion capture (of CO_2)
TOC = total organic carbon

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Chapter 4: Monitoring MEA degradation

Evaluation of methods for monitoring MEA degradation during pilot scale post-combustion capture of CO_2

Chapter 4 contains the manuscript of a paper that has been submitted to the *International Journal of Greenhouse Gas Control* in 2015. The full citation for this paper is:

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This manuscript discusses the changes in the functional groups of the organic compounds in the MEA absorbent during the pilot campaign at CSIRO's PCC pilot plant at Loy Yang using well established elemental and spectroscopic techniques. This chapter contributes directly to aim C and provides important information for aims A and B.

Declaration for Thesis Chapter 4

Declaration by candidate

In the case of Chapter 4, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Defined the aims and scope of the manuscript, conducted all the laboratory work, wrote the initial draft of the paper and coordinated feedback and comments from all authors.	80

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
T. Vincent Verheyen	Provided valuable advice on the use and interpretation of data presented in this manuscript. Provided valuable advice on the structure, content and presentation of the manuscript.	N/A
Samuel B. Adeloju	Valuable advice on the structure, content and presentation of the manuscript. Co-ordinated submission and revision of the article	N/A
Erik Meuleman	Provided the sample set and associated pilot plant operation data. Provided valuable comments on the final drafts.	N/A
Alan L. Chaffee	Valuable input into final drafts	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature	A. Reynolds	**Date** 31-Mar-2015
Main Supervisor's Signature		**Date** 31|3|15

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

Evaluation of methods for monitoring MEA degradation during pilot scale post-combustion capture of CO_2

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ABSTRACT

Amine degradation is an important and current focus in the development of chemical absorption technology based on the use of aqueous amines for post-combustion capture (PCC) of CO_2. The oxidative degradation and carbamate polymerisation of monoethanolamine (the current industry standard amine for PCC) has been studied extensively at the laboratory scale. However, methods for monitoring long-term amine degradation during pilot, demonstration and commercial scale PCC are needed to enable researchers and operators to optimise amine management (e.g. minimising degradation and optimising reclamation strategies), improve PCC plant operation and avoid operational instabilities. The current industry standard method, based on the measurement of heat-stable salts (HSS) is not suitable for continuous monitoring of amine degradation. This study discusses the organic structural changes of severely degraded 30% (w/w) aqueous monoethanolamine samples obtained from a PCC pilot plant operating at a brown coal-fired power station in Australia. It demonstrates that absorbance measurement at 313 nm by UV-Vis, change in infra-red absorbance and the organic carbon content of degradation products correlate strongly with HSS concentrations. These parameters are easily measured using well established technology and are suitable for monitoring the degradation of aqueous monoethanolamine during PCC.

Keywords: post-combustion capture of CO_2, monoethanolamine, coal-fired flue gas, heat-stable salts, degradation

Highlights:

- MEA degradation during pilot-scale PCC of CO_2 is characterised
- Total carbon and NMR estimated more MEA degradation than HSS
- MEA degradation can be monitored using UV-Vis, ATR-IR or total carbon analysers

1. INTRODUCTION

Chemical absorption with aqueous amine absorbents is the current industry standard for post-combustion capture (PCC) of CO_2 from coal-fired power station flue gas (International Energy Agency, 2012; International Energy Agency, 2013; Boot-Handford et al., 2014). This gas separation technology is suited to the low CO_2 partial pressure and high moisture content of typical flue gases (Kohl and Nielsen, 1997). Despite substantial progress in recent years, a number of challenges for commercial-scale operation remain (International Energy Agency, 2012; International Energy Agency, 2013; Boot-Handford et al., 2014). For example, corrosion and degradation of the aqueous amines are still significant challenges for these PCC systems despite development of low corrosivity, degradation resistant absorbents (Knudsen et al., 2009; Nainar and Veawab, 2009). Managing amine degradation is crucial for (i) minimising potential human and environmental impacts; (ii) maintaining operational stability and energy efficiency of PCC processes; and (iii) minimising the need for amine reclamation and disposal (Reynolds et al., 2012; Léonard et al., 2014). However, there is a clear need to identify simple, rapid measurement techniques that could be used to monitor the accumulation of aqueous amine degradation products. This would enable amine degradation to be managed proactively during PCC at pilot, demonstration and commerical scales.

Research into degradation of aqueous amines has focussed on three key pathways: oxidative degradation; formation of heat-stable salts (HSS); and carbamate polymerisation or thermal degradation (Gouedard et al., 2012; Vega et al., 2014). Oxidative degradation is the most rapid amine degradation pathway during PCC and is driven by both the reactivity of amines and the high oxygen content [typically 4-5%, (Kittel et al., 2012)] of flue gases. Dissolved metals (from corrosion and fly ash intrusion) are also known to catalyse oxidative degradation in aqueous amines (Goff and Rochelle, 2004; Goff and Rochelle, 2006). One of the main products of oxidative degradation are organic acids (eg. formate, acetate and oxalate) which condense with amines to form amides (Lepaumier et al., 2011; Gouedard et al., 2012). These amides contribute to HSS because they are not hydrolysed during CO_2 desorption (Gouedard et al., 2012). SO_x from the flue gas are readily oxidised to sulfate, which also form HSS with aqueous amines (Reynolds et al., 2012; Beyad et al., 2014). Sulfate accumulation is usually minimised by scrubbing the flue gas with dilute sodium hydroxide upstream of the PCC process (Knudsen et al., 2009; Beyad et al., 2014). Carbamate polymerisation is also refered to as thermal degradation because it is most rapid during CO_2 desorption (Davis and Rochelle, 2009; Lepaumier et al., 2009; Gouedard et al., 2012). Carbamate polymerisation is considered to be a minor contributor to amine degradation (Léonard et al., 2014).

HSS are an important subset of degradation products because: (a) amines that have been oxidised and (b) those that have formed salts with inorganic or organic anions are not available to capture CO_2. Currently, the HSS concentration is used as the main indicator of amine degradation (Kohl and Nielsen 1997; Knudsen et al., 2009; Mangalapally and Hasse, 2011; Meuleman et al., 2011). However, the measurement of HSS is a labour intensive process involving cation exchange and acid-base titration (Vevelstad et al., 2013) to determine the charge equivalent of acidic anions (Knudsen et al., 2009). The two primary sources of HSS anions (oxidative degradation and accumulation of SO_x and NO_x) can be investigated by measuring the concentrations of individual anions by ion chromatography (Kohl and Nielsen, 1997; Sexton and Rochelle, 2011; Vevelstad et al., 2013). Both HSS and ion chromatography provide valuable information about amine degradation, but neither is rapid, simple or readily adapted to on-line or at-line monitoring.

Conceptually, it may be possible to rapidly assess the severity of amine degradation with minimal interferences from accumulation of minerals and inorganics by measuring the portion of carbon or nitrogen associated with intact and degraded amine molecules. This approach is indeed quite feasible as well established techniques are available for measuring total nitrogen and total organic carbon (TOC) (Siegmann-Hegerfeld et al., 2013; Ge et al., 2014).

Spectroscopic techniques such as UV-Vis (ultraviolet and visible light spectroscopy), ATR-IR (attenuated total reflectance – infra red spectroscopy) and ^{1}H NMR (proton nuclear magnetic resonance) have the potential to provide rapid information about the condition of the aqueous amine during PCC (Dickens, 2010). The ability of ATR-IR spectroscopy to measure amine concentrations and CO_2 loadings (Geers et al., 2011; Richner and Puxty, 2012) in addition to assessing absorbent condition has been previously demonstrated (Einbu et al., 2012). ^{1}H and ^{13}C NMR have previously been used to identify organic degradation products of 30% (w/w) MEA in the presence of iron (Ciftja et al., 2012), suggesting that NMR may also be useful for monitoring the accumulation of organic degradation products during PCC

The practice of assessing amine condition by visual inspection of the colour of the aqueous amine (Blachly and Ravner, 1966; Kohl and Nielsen, 1997) and the observations of colour changes during laboratory-scale degradation experiments (Bougie and Iliuta, 2014; Léonard et al., 2014) strongly suggest that UV-Vis spectroscopy may be a useful tool for assessing the condition of aqueous amine absorbents. Furthermore, amine degradation interfered with the use of UV-Vis for monitoring amine concentrations and CO_2 loadings (van der Ham et al., 2014; van Eckeveld, et al., 2014), indicating that UV-Vis is more sensitive to amine degradation than amine concentration or CO_2 loadings.

In this study, we employ various methods, such as TOC, UV-Vis, ATR-IR and NMR, to: (i) investigate the changes in the organic composition of aqueous monoethanolamine (MEA) during pilot-scale PCC, and (ii) evaluate the potential for these methods to provide rapid and reliable information that could be used to facilitate improved amine management (e.g. minimising degradation and optimising reclamation strategies), better PCC plant operation and avoidance of operational instabilities. These methods are evaluated using twelve samples of 30% (w/w) aqueous MEA obtained during a six month PCC campaign at CSIRO's pilot plant at AGL's Loy Yang brown coal-fired power station. The absorbent was used for PCC for more than 700 h prior to the beginning of this campaign to minimise the introduction of any biases or influences associated with the use of fresh, undegraded amine.

2. METHODS AND MATERIALS

2.1 Sample set

A single batch of 30% (w/w) MEA was prepared and used to capture CO_2 at two PCC pilot plants as described previously (Reynolds et al., 2014). Briefly, the 30% (w/w) MEA was used to capture 42 t CO_2 over 733 h at a PCC pilot plant operated by CSIRO at Stanwell's 1400 MW black coal-fired power station in Queensland, Australia. The aqueous amine was then stored in a plastic intermediate bulk container (IBC) for 18 months before being used to capture CO_2 at CSIRO's PCC pilot plant at AGL's 2210 MW brown coal-fired power station in Victoria, Australia. No oxidation or corrosion inhibitors were added to the absorbent and the aqueous amine was not filtered, distilled or otherwise reclaimed. A slip-stream of flue gas from the power station was scrubbed with dilute sodium hydroxide prior to entering the absorber train. The SO_2 concentration of the flue gas entering the absorber exceeded 8.5 ppm (wet volume basis) less than 10% of the time. During the campaign at Loy Yang, twelve samples of lean aqueous MEA absorbent were collected in high density polypropylene (HDPE) bottles, immediately transferred to a laboratory and stored in the dark at -20°C. Details of these twelve samples are given in Table 1.

2.2 Pilot plant operation

Details of CSIRO's pilot plant at Loy Yang, including the on-line gas analyser used to measure SO_2 concentrations and the CO_2 product stream flow meter, are given elsewhere (Artanto et al., 2012). Details of a concurrent pilot plant campaign are described by Azzi et al. (2014). At the beginning of the pilot plant campaign at Loy Yang, the target parameters were 80% CO_2 capture, liquid:gas (L/G) ratio of approximately 4 and flue gas flow rate of 125 kg/h. During the PCC campaign, the L/G ratio was decreased to approximately 2 to maintain stable pressure drops across the absorber columns. As a result, the CO_2 capture efficiency decreased to approximately 60%. The absorbent temperature at the absorber inlet was 40°C throughout the campaign and the desorber bottoms temperature increased slightly from approximately 114°C to 116°C. The campaign was conducted during spring and summer (August 2012 to January 2013) and the effects of the local weather were evident in the increase of the flue gas temperature at the absorber inlet from approximately 28°C to approximately 35°C.

Table 1. Descriptions of the aqueous MEA samples obtained from CSIRO's pilot plant at Loy Yang

Operating hours	CO_2 captured at Loy Yang (t)	MEA concentration (% w/w)	CO_2 content (mol CO_2/kg)	CO_2 lean loading (CO_2: MEA molar ratio)	Heat Stable Salts (% w/w, as MEA)
5	0.12 ± 0.0001	35.2* ± 0.6	1.22 ± 0.01	0.212 ± 0.1	0.797 ± 0.03
57	1.15 ± 0.001	30.3 ± 0.6	1.36 ± 0.01	0.274 ± 0.1	0.905 ± 0.03
113	2.41 ± 0.003	31.6 ± 2	1.21 ± 0.007	0.234 ± 0.3	0.971 ± 0.03
189	3.85 ± 0.005	27.3 ± 0.2	0.962 ± 0.02	0.216 ± 0.06	1.05 ± 0.02
242	4.91 ± 0.006	27.4 ± 0.7	0.963 ± 0.005	0.214 ± 0.1	1.05 ± 0.01
309	6.04 ± 0.008	30.7 ± 0.09	1.1 ± 0.004	0.219 ± 0.03	1.23 ± 0.02
372	7.26 ± 0.009	28.5 ± 0.4	1.06 ± 0.007	0.227 ± 0.08	1.34 ± 0.06
506	9.81 ± 0.01	30.8 ± 0.8	0.676 ± 0.0007	0.134 ± 0.1	1.39 ± 0.05
557	10.6 ± 0.01	26.9 ± 0.5	0.656 ± 0.001	0.149 ± 0.08	1.52 ± 0.04
677	12.1 ± 0.02	28.3 ± 0.6	0.768 ± 0.003	0.166 ± 0.1	1.76 ± 0.01
800	13.7 ± 0.02	26.9 ± 0.8	0.475 ± 0.002	0.108 ± 0.1	2.03 ± 0.06
834	14.1 ± 0.02	27.4 ± 1	0.587 ± 0.007	0.131 ± 0.2	2.29 ± 0.01

*This concentration was not included in statisical calcuations or correlations because because the measured concentrations was subject to matrix interferences (Reynolds et al., 2014).

2.3 MEA concentration

MEA concentrations were determined using a GC-FID method discussed in detail elsewhere (Reynolds, Verheyen et al. 2014). In summary, samples were diluted 1:1000 (1:10 by mass and 1:100 by volume) in 0.1% ammonium hydroxide (BDH Chemicals, approximately 35% (w/w)) and 25 mg/L d_5-pyridine (internal standard, Cambridge Isotope Laboratories, 99.5%) in deionised water (18.2 MΩ/cm, MilliQ Academic, Millipore). Standards and reagents were obtained from Chem Supply (MEA, >99% purity), BDH chemicals [ammonium hydroxide, approximately 35% (w/w)] and Cambridge Isotope laboratories (d_5-pyridine, 99.5%).

The GC-FID (gas chromatography with flame ionisation detection, CP3800 Varian, CA) conditions used were: 15 m, 0.53 mm ID, thick film (1.5 µm) 5% phenyl 95% dimethylsiloxane column (SGE, Melbourne, Australia), 0.3 µL injection, 260°C injector temperature, 1177 injector, SGE focus liner, 1:10 split, 335°C detector temperature and an electronic flow controller delivering 2.8 mL/min helium carrier gas with a 2.0 psi pressure pulse for 0.25 min after injection. The column oven program was 70°C for 1 min, ramp to 100°C at 10°C/min, ramp to 320°C at 20°C/min and hold for 3 min. The MEA concentration of the sample obtained after capturing 0.12 t CO_2 was included in statistical calcutations because the measured concentrations was subject to matrix interferences (Reynolds et al., 2014).

2.4 Heat stable salts (HSS)

Approximately 1 g (weighed to ± 0.002 g) of sample was weighed into a 100 mL beaker. 10 (± 0.2) mL of Dowex 50W-X8 (50-100 mesh, protonated form, Sigma Aldrich), a magnetic stirrer bar and approximately 50 mL deionised water (18.2 MΩ/cm resistance, MilliQ Academic, Millipore) were added. The mixture was stirred at 70°C-75°C for 45 min. After cooling, the supernatant was poured through a PTFE filter (0.2 µm, Advantec, Japan) into a 500 mL beaker. The resin was rinsed three times by adding 100 mL deionised water, stirring for 5 min, settling and pouring the supernatant through the PTFE filter into the 500 mL beaker. The combined supernatants were titrated against 0.01 N NaOH (Rowe Scientific) . The sodium hydroxide solution was standardised against potassium hydrogen phthalate (Sigma Aldrich, >99.95%) and the moles of base consumed were converted to a mass of MEA.

The practical quantitation limit (PQL) of 0.13% (w/w, as MEA) was calculated from the Student's *t* value (99% confidence, one-tailed) multiplied by the standard deviation of seven replicates of a 0.462% (w/w, as MEA) standard containing 1.53 mg/g acetic acid (Ajax finechem, >99%) and 3.56 mg/g Na_2SO_4 (BDH Chemicals, >99%) in 30% (w/w) MEA (2-aminoethanol Chem Supply, >99%).

2.5 Total organic carbon (TOC) and inorganic carbon

The details of total carbon, inorganic carbon and total organic carbon analyses are given elsewhere (Reynolds, Verheyen et al. 2014). Each sample was diluted by mass and analysed using a Shimadzu TOC-V analyser (Japan). The difference between total carbon and inorganic carbon (TOC, total organic carbon) was expressed as % MEA (w/w) to enable comparison with MEA and HSS concentrations.

2.6 UV-Vis

Each sample was diluted to between 1:250 and 1:1250 in deionised water (18.2 MΩ/cm, MilliQ Academic, Millipore) to obtain an absorbance between 0.2 and 0.6 in the region of interest (250 nm to 400 nm). Absorbance spectra were measured between 190 nm and 900 nm in a 1 cm quartz cell using a Varian Cary 300 (Australia) UV-Vis spectrophotometer.

2.7 Nuclear Magnetic Resonance (NMR)

Diethanolamine (99%), N-acetylethanolamine (technical grade), N-(2-hydroxyethyl)-2-imidazolidione (75% in water), 1-(2-hydroxyethyl)succinimide (95%), 1-(2-hydroxyethyl)imidazole (97%), N,N-bis-(2-hydroxyethyl)oxamide (98%) and bicine (>99%) were obtained from Sigma Aldrich, Australia. Chromatography grade 2-oxazolidione was obtained from Wako Pure Chemical Industries (>97%). Between 50 and 100 mg of each standard (except diethanolamine) was accurately weighed and dissolved in 1 g of 30% (w/w) MEA. Diethanolamine (DEA) was diluted in deionised water after weighing because the chemical structure and NMR spectra of DEA are very similar to MEA. The structures of these compounds are shown in Figure 1.

500 µL D_2O containing an internal standard (TMSP, trimethylsilyl propionic acid) was added to 1 g of each sample and standard solution. Proton NMR (with suppression of the water resonances) and ^{13}C NMR (with broadband proton decoupling) spectra were recorded using a 600 MHz Bruker NMR with the parameters in Table 2. Both proton and ^{13}C NMR spectra were recorded for all samples. DEPT (distortionless enhancement by polarization transfer) NMR spectra were also obtained for three samples. Only proton NMR spectra were recorded for the standards.

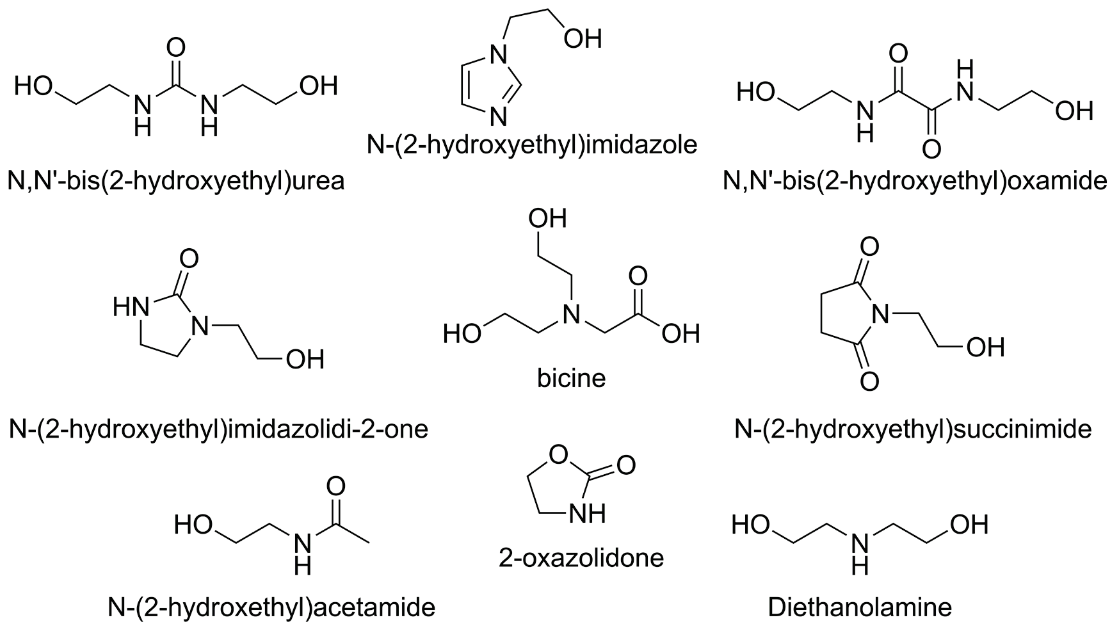


Figure 1. The structures of the organic degradation products analyzed by NMR

Table 2. NMR analysis parameters

Description	**^{1}H NMR**	**^{13}C NMR**
Temperature	303 K	303 K
Number of scans	40	800
Acquisition time (s)	4.5	0.865
Relaxation delay (s)	4	4
Dwell time (µs)	69	13.2

2.8 Attentuated Total Reflectance – Infra-Red (ATR-IR)

A drop of sample was placed on the diamond crystal of a Specac Golden Gate Mark II ATR accessory (UK) and spectra were recorded with a Varian FTS1000 FTIR (MA). The optics and ATR accessory were purged with dry nitrogen during spectra acquisition. 256 scans with 4 cm^{-1} resolution were averaged and all spectra were corrected for attenuation using Varian Resolutions software. The most informative difference spectra were obtained by subtracting a 30% MEA spectrum from each absorbent spectrum. To avoid creating spectral artifacts, the 30% MEA spectrum was multiplied by 0.9 prior to the subtraction.

2.9 Statisitical methods

Unless specified below, measurements were conducted in triplicate. Error bars and uncertainty intervals were calculated as mean deviations (MD) with a coverage factor of one. Uncertainty intervals for calculated values (eg. CO_2 lean loading) were estimated by the sum of MDs. Student's *t* tests and Pearson's correlation co-efficients were calculated using IBM SPSS Statistics (version 20.0.0).

Operating hours was defined as the number of minutes the flue gas blower flow rate was greater than zero and uncertainty was not estimated. The CO_2 captured was calculated as the sum of the flow rate downstream of the desorber off-gas condenser measured at one minute intervals. Uncertainty was estimated as the sum of the manufacturer's uncertainty guarantee (±0.125%) of each measurement. Proton NMR and ^{13}C NMR measurements were obtained from single spectra. Uncertainty for ^{1}H NMR was estimated from triplicate measurements of the sample obtained after capturing 7.62 t CO_2. No uncertainty estimates were calculated for ^{13}C NMR data.

3. RESULTS

3.1 Heat stable salts (HSS)

Figure 2 shows a steady increase in the HSS concentration during the pilot plant campaign. HSS is the total molar concentration of anions expressed as a mass of MEA and is the current industry standard measure of amine degradation. HSS includes organic and inorganic anions, but excludes carbonates because they are converted to gaseous CO_2at the pH of the cation exchange resin. Figure 2 shows the indicative reaction rate (k, assuming pseudo first order kinetics with respect to CO_2 captured) was 0.067 per t CO_2 captured, indicating that HSS concentration doubled for every 10 t CO_2 captured during this campaign.

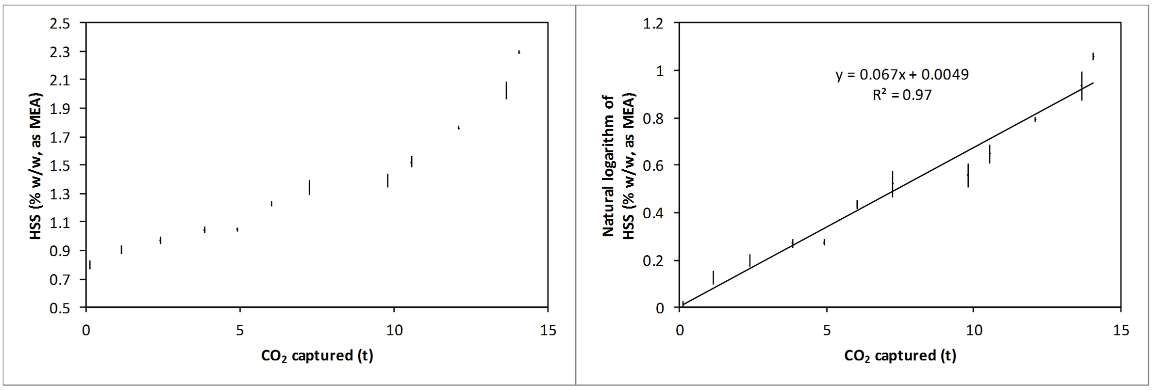


Figure 2. Accumulation of heat-stable salts (HSS) during the PCC campaign at Loy Yang

3.2 UV-Vis

The UV-Vis spectra of MEA absorbent samples in Figure 3a reveal very little absorbance at visible wavelengths above 400 nm, however, strong absorbance occurs in the near UV region. This absorbance is consistent with the orange-red colour of the samples (Figure 3b). The shape of the absorbance spectra indicate the presence of two absorption bands above 200 nm, which are typical of the $\pi \rightarrow \pi^*$ transitions of simple aromatic systems. The inflection points (278 nm and 305 nm) were identified from the first derivatives of three-point average smoothed UV-Vis spectra because the second derivative plots were too noisy to enable reliable identification of the wavelength of the stationary points. Both heterocyclic aromatic compounds and carbonyl functional groups typically absorb light between 200 and 350 nm. N-(2-hydroxyethyl)imidazole is a heterocyclic aromatic compound that has been widely identified as a product of oxidative degradation (Gouedard et al., 2012; Vevelstad et al., 2013) and has been identified in degraded aqueous MEA used in a pilot plant (da Silva et al., 2012). The sequential additions of N-(2-hydroxyethyl)imidazole to the most aged sample in Figure 3c indicate that this compound is very likely to be a significant contributor to the UV-Vis spectra of these samples. The inflection points in Figure 3c remained at 278 nm and 305 nm but the addition of N-(2-hydroxyethyl)imidazole enabled two maxima (270 nm and 313 nm) to be identified. The molar absorptivity of N-(2-hydroxyethyl)imidazole added to the most aged sample was 12 $M^{-1}cm^{-1}$ at 270 nm and 8.0 $M^{-1}cm^{-1}$ at 313 nm.

Absorbtivity of the aqueous MEA absorbent samples at 270 nm, 278 nm, 305 nm and 313 nm are strongly correlated and Figure 4 shows the strong correlation between HSS concentration and the absorbtivity of the absorbent samples at 313 nm. The strong correlations of absorbtivity with HSS and identification of contribution from an oxidative degradation product (N-(2-hydroxyethyl)imidazole) strongly suggests that UV-Vis absorbance at suitable wavelengths is a rapid and useful measurement for assessing amine degradation.

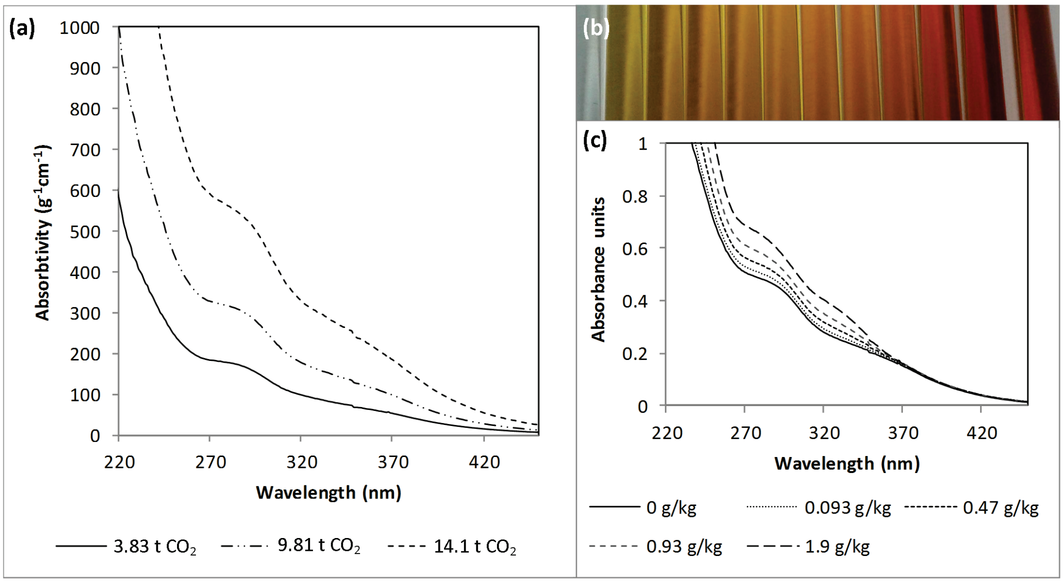


Figure 3. (a) UV-Vis spectra of three samples; (b) photo of 30% MEA (left) and 12 samples of increasingly degraded 30% MEA; and (c) UV-Vis spectra of N-(2-hydroxyethyl)imidazole added to the most aged pilot plant sample.

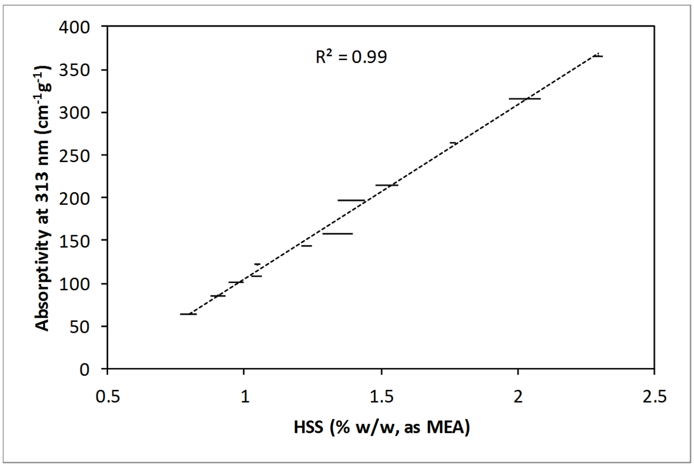


Figure 4. Strong linear correlation between absorbance at 313 nm and the HSS concentration

3.3 Inorganic and organic carbon

The inorganic carbon concentration is a direct measure of the CO_2 evolved by acidification of the sample and includes CO_2 liberated from dissolved carbonates as well as carbamate. CO_2 content correlated more strongly with HSS (*r*=-0.861, significant at the 0.01 level) than MEA concentration (*r*=0.474, not significant at the 0.05 level). The average CO_2:MEA molar ratios ranged from 0.11 to 0.27, which are in the typical lean CO_2 loading range for PCC. Despite the conservative uncertainty estimates for CO_2 loading, both the CO_2 concentration (as mg/kg, Figure 5) and the lean CO_2 loading (as CO_2:MEA molar ratio, Figure 6) of the amine decreased during this campaign. This is consistent with the increasingly severe CO_2 desorption due to changes in the operating conditions (e.g. decrease in absorbent flow and slight increase in desorber bottoms temperature) as well as decreased capacity of the absorbent to absorb CO_2 due to amine degradation and accumulation of HSS.

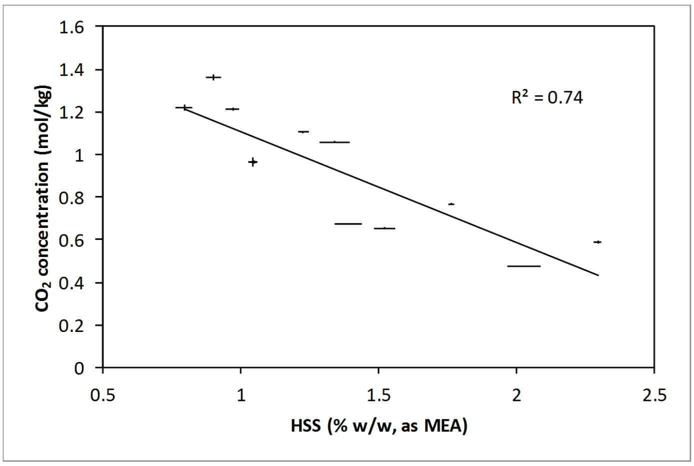


Figure 5. Change in CO_2 content with increasing HSS concentration

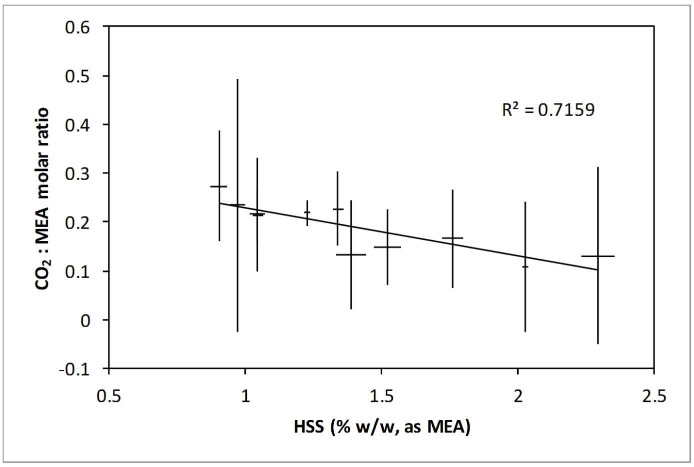


Figure 6. Change in CO_2 lean loading with increasing HSS concentration

Previous work demonstrated a statistically significant difference between the total organic carbon concentration (TOC, expressed as % MEA (w/w)) and the MEA concentration (Reynolds et al., 2014). This difference is easily measured and may be a useful way to determine the concentration of "organic degradation products" without interference from SO_x, NO_x and other inorganic anions. The strong correlation between HSS and organic degradation product concentrations in Figure 7 is further evidence that this technique may be useful for monitoring degradation of aqueous amines during PCC.

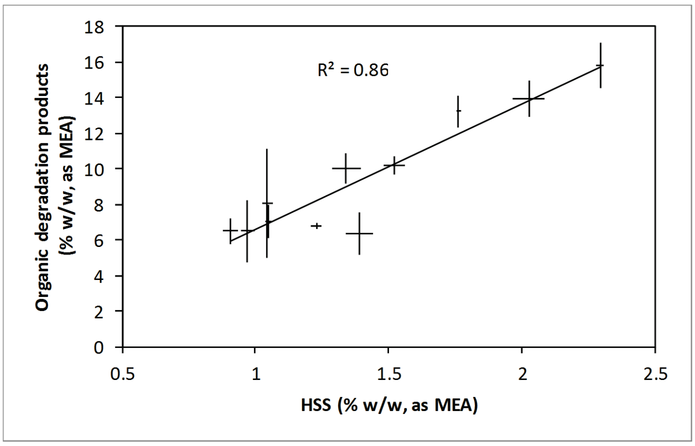


Figure 7. Correlation between organic degradation products and HSS concentration

3.4 ATR-IR

Infra-red absorbance by water, MEA and carbamate species dominate the ATR-IR spectra in Figure 8, top. However, small changes in the O-H and N-H stretch region (2600 to 3700 cm^{-1}) and fingerprint region (900 to 1700 cm^{-1}) are evident after subtracting a 30% MEA spectrum from each sample (Figure 8, bottom). Changes in the shape of the absorbance bands between 2600 and 3700 cm^{-1} are consistent with changes in the inter- and intramolecular hydrogen bonding environment as well as changes in hydroxyl and amino functional groups due to carbamate formation, MEA degradation and changes in pH or alkalinity. Changes in the intensities of peaks between 900 and 1700 cm^{-1} are dominated by changes in the concentrations and ratios of carbamate and MEA. However, the absorbance bands at 1629 cm^{-1} and 1568 cm^{-1} may be indicative of carbonyl functional groups typical of amine degradation products including amides [carbonyl stretch (3680 and 1630 cm^{-1}) and NH bend (1640-1550 cm^{-1})].

Subtracting a 30% MEA spectrum from the sample spectra generated strong regression coefficients (R^2>0.9) between ATR-IR intensities at 1629, 1602, 1639 cm^{-1} and 1488 cm^{-1} and the HSS concentration or the CO_2 content (Figure 9). The peak at 1488 cm^{-1} has previously been identified as a carbamate stretch (Richner and Puxty, 2012) and correlated strongly with the CO_2 content and weakly with HSS concentration in these pilot plant samples. The valley at 1602 cm $^{-1}$ and the peak at 1629 cm^{-1} both correlated strongly with the HSS concentration. The intensity of the valley at 1602 cm^{-1} was determined by a peak at 1600 cm,$^{-1}$ which has been assigned to the amino scissor vibration of free MEA by Richner and Puxty (2012). The peak at 1629 cm^{-1} is close to the NH_3^+ asymmetric wag (Richner and Puxty, 2012) but may also be influenced by amide N-H bending or C=O stretch.

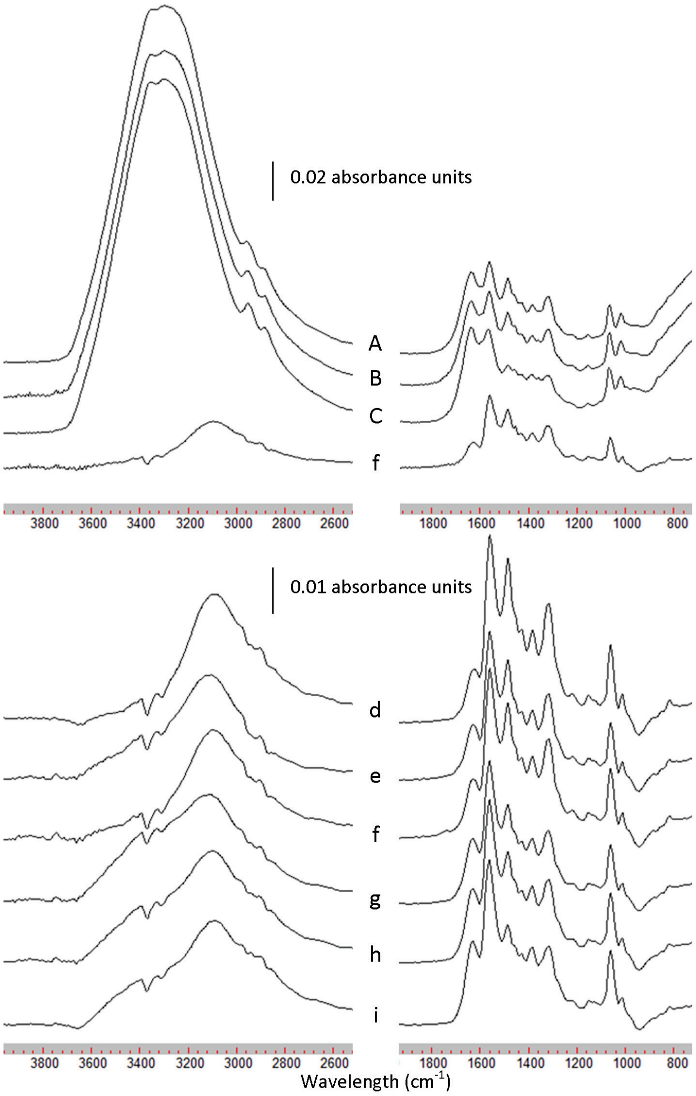


Figure 8. Stretch and fingerprint regions of ATR-IR spectra. A, 0.12 t CO_2; B, 6.04 t CO_2; C, 14.1 t CO_2; d, 1.15 t CO_2; e, 3.85 t CO_2; f, 6.04 t CO_2; g, 9.81 t CO_2; h, 12.1 t CO_2; and i, 14.1 t CO_2. Lower case letters (d-i) are the difference between the sample and 90% of the 30% (w/w) spectra.

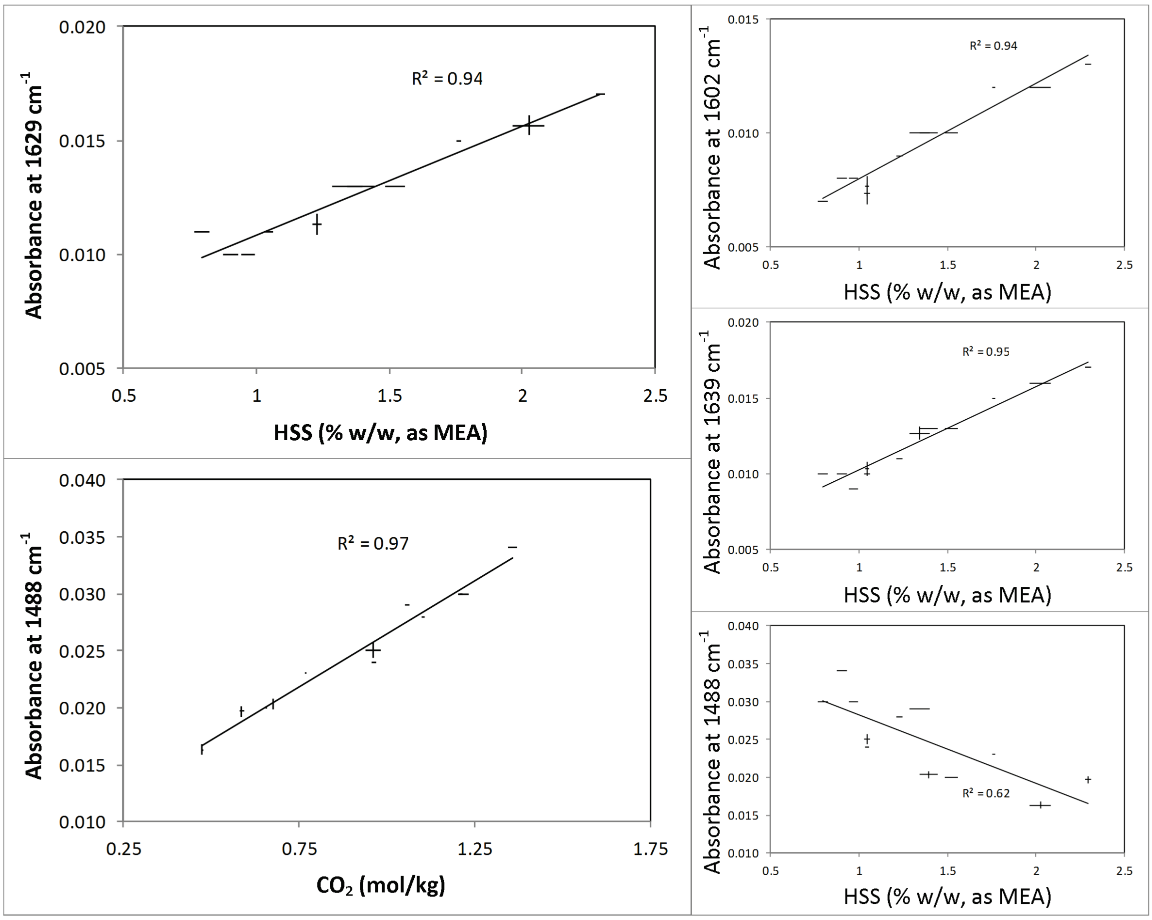


Figure 9. Correlations between absorbance of ATR-IR difference spectra and HSS or CO_2 concentrations

3.5 ^{1}H NMR and ^{13}C NMR

The MEA and MEA-carbamate α-amino and α-hydroxyl proton and carbon resonances are major contributors to the ^{1}H and ^{13}C NMR spectra in Figures 10 and 11. Notably, the resonances of MEA and MEA-carbamate are consistent with previously reported spectra (Bottinger et al., 2008). The alcohol and amine protons are silent due to rapid exchange in the aqueous amine. The shifts for α-amino and α-hydroxyl nuclei for MEA and protonated MEA are observed as the average of MEA and $MEAH^+$ due to rapid proton exchange in the aqueous system at room temperature. Resonance of MEA-carbamate ($-CO_2$) carbon are also evident in the ^{13}C NMR spectra at 164.5 ppm. Amine degradation is evident from increasing complexity in the α-hydroxyl and α-amino resonance regions.

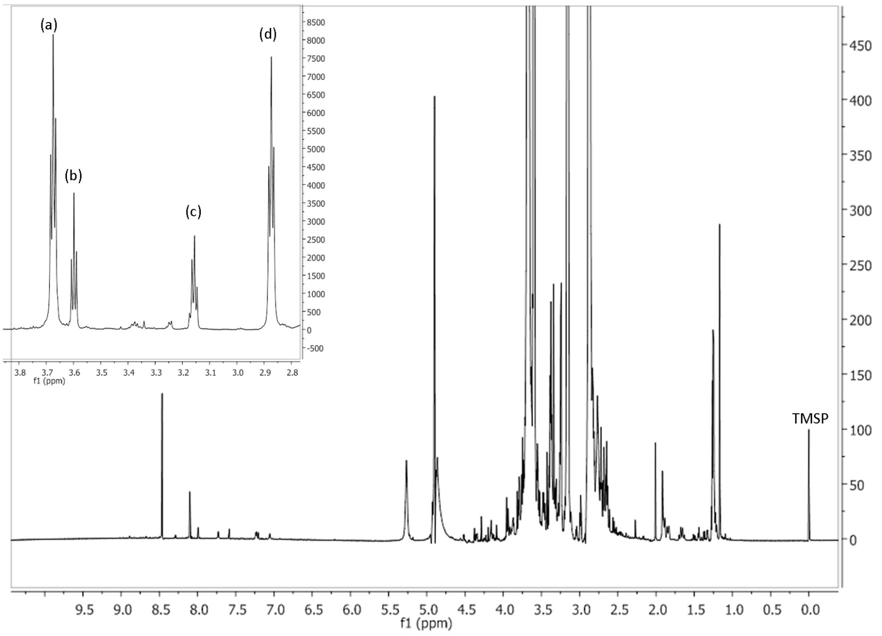


Figure 10. ^{1}H NMR spectrum of the earliest sample (0.12 t CO_2). Insets show MEA and MEA-carbamate resonances. (a) MEA and MEAH$^+$ α-OH, (b) MEA carbamate α-OH, (c) MEA carbamate α-NH, (d) MEA and MEAH$^+$ α-NH, TMSP is the internal standard.

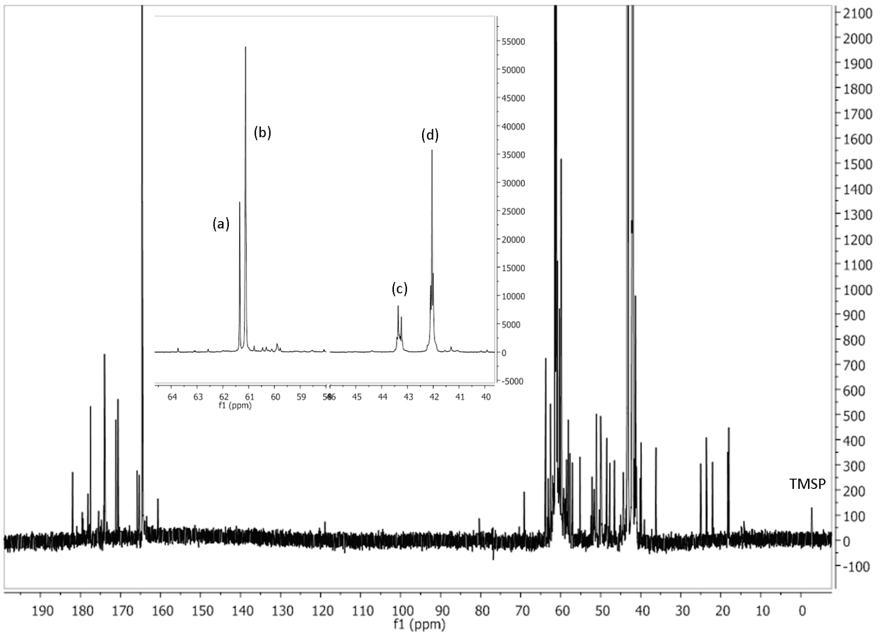
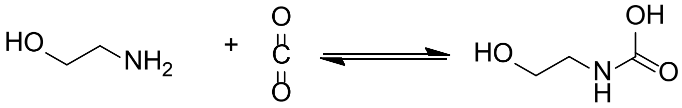


Figure 11. Typical ^{13}C NMR spectrum of the earliest sample (0.12 t CO_2). Insets show MEA and MEA-carbamate resonances. (a) MEA and MEAH$^+$ α-OH, (b) MEA carbamate α-OH, (c) MEA carbamate α-NH, (d) MEA and MEAH$^+$ α-NH, TMSP is the internal standard.

The spin-spin splitting patterns of the ^{1}H NMR spectra are consistent with traditional rules and previously reported spectra (Bottinger et al., 2008; Perinu et al., 2014). However, splitting of the ^{13}C MEA resonances has not been previously reported. The resonances of the ^{13}C nuclei at the α-amino position of MEA was split into a doublet with 18 Hz separation. The MEA carbamate α-amino was splitting was more complex and the DEPT spectra separated the splitting pattern into a positive 18 Hz doublet superimposed on a negative 18 Hz triplet. The orientations of the peaks in the DEPT spectra indicated that that the 18 Hz triplet was generated by MEA-carbamate ^{13}C nuclei with two protons while the 18 Hz doublets in both the MEA and MEA-carbamate were generated by ^{13}C nuclei with either one or three protons. This suggests that the α-amino carbons in the MEA and MEA-carbamate species may have exchanged with protons and deuterium in the 1:1 H_2O:D_2O solvent.

One probable cause of the 18 Hz separation of the α-amino ^{13}C resonances of both MEA and MEA-carbamate is chemical exchange. The observation of peak broadening in some spectra recorded at 30°C indicates that these ^{13}C NMR spectra were acquired between “slow exchange” and coalescence conditions. For this reason, the 18 Hz separation could be caused by chemical exchange with a rate greater than 18 s^{-1} at about 30°C. The interferograms were recorded at 136 µs intervals, indicating that the maximum reaction rate that could be observed in these NMR spectra is 75 s^{-1}. The reversible reaction between MEA, aqueous CO_2 and the carbamic acid (Reaction 1) of MEA satisfies these criteria because (a) the reaction rate for the hydrolysis of MEA carbamic acid is approximately 30 s^{-1} at 30°C (McCann et al., 2009) and (b) the second order reaction rate for condensation of MEA and aqueous CO_2 is likely to be limited by the CO_2 concentration in these lean samples.



Reaction 1. Reaction between MEA, aqueous CO_2 and carbamic acid (after McCann et al., 2009)

The ratio of carbamate to MEA calculated from the ratio of both the α-hydroxyl and α-amino proton NMR integrals of ^{1}H NMR spectra is shown in Figure 12. Despite overlapping of the α-hydroxy MEA and carbamate peaks, there was a strong correlation (*r*=0.987) and no significant difference (paired Student’s *t* test, 95% confidence interval -0.013 to 0.008, 0.625 two-tailed significance level) between the ratios of the α-hydroxy or α-amino proton resonances. However, despite strong correlation (*r*=0.991 for α-amino and *r*=0.980 for α-hydroxyl), Student’s *t* -tests demonstrated that both ratios were significantly ($p<0.01$) larger than the CO_2 loading calculated from the CO_2 content (measured by TOC) and the MEA concentration (measured by GC-FID). This may be because the MEA concentration measured by ^{1}H NMR excludes MEA present as HSS.

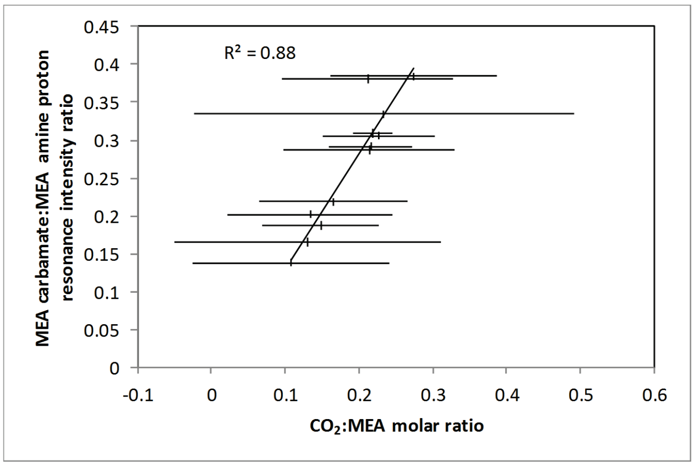


Figure 12. Correlation between CO_2 molar loading (measured by GC-FID and TOC) and Carbamate:MEA ratio measured by ^{1}H NMR

Both proton and carbon NMR resonances, other than MEA and MEA carbamate α-amino and α-hydroxyl protons, were classified as: (i) aliphatic resonances (^{1}H NMR: complex between 1 and 2.5 ppm, ^{13}C NMR: well resolved between 15 and 35 ppm); (ii) complex unresolved resonances close to MEA and MEA carbamate peaks; and (iii) well resolved carbonyl, amide and aromatic resonances (^{1}H NMR: 5 to 9 ppm, ^{13}C NMR: 160 to 185 ppm). Resonance for the carbonates and carbamate are also evident in the ^{13}C NMR between 160 to 170 ppm. Unlike the ^{13}C NMR experiments in this report, ^{1}H NMR is quantitative and the integrals of these regions are could be used to monitor amine degradation.

The ^{1}H NMR resonances of a range of degradation products in 30% (w/w) MEA were equivalent to those previously reported by Ciftja et al. (2012). The majority of the proton resonances of these compounds were in the α-hydroxy and α-amino ranges of MEA and MEA-carbamate. Very few alkyl, aromatic or carboxyl characteristic resonances were observed in Figure 10.

With the exception of bicine, the resonances of α-amino and α-hydroxyl protons of all compounds shifted downfield to some extent. The α-amino proton resonances for primary and secondary ethanolamines (e.g. diethanolamine and bicine) shifted downfield less than 0.1 ppm. The α-hydroxyl downfield shifts of DEA and bicine were larger than the α-amino downfield shifts for DEA and bicine, but did not exceed 0.2 ppm. These small downfield shifts of these α-amino and α-hydroxyl protons suggest that ^{1}H NMR is unlikely to be sensitive to MEA disproportionation reactions. Downfield shifts of between 0.5 and 1 ppm were observed for α-amino protons in the condensation products of a carboxylate (eg. acetate or oxamide) and MEA or DEA. Small downfield shifts (<0.15 ppm) were also evident in compounds for α-hydroxy protons relative to MEA. This indicates that condensation products of carboxylates from oxidative degradation of MEA are likely to contribute to ^{1}H NMR resonance downfield of MEA α-amino and α-hydroxyl.

The cyclic amide 2-oxazolidone has been widely reported as a key intermediate of carbamate polymerisation and the both α-hydroxy and α-amino resonances are shifted further downfield (0.8-1 ppm) than oxidative degradation products relative to MEA. However, 2-oxazolidone resonances are difficult to distinguish from oxidative degradation products because these shifts are relatively small and the MEA/MEAH$^+$ resonance shift is dependant on pH. In ^{1}H NMR spectra of MEA absorbent samples, the MEA and MEAH$^+$ α-amino shift ranged from 2.85 to 2.9 ppm and α-hydroxyl shift ranged from 3.65 to 3.7 ppm.

Figure 13c shows that the complex aliphatic resonances between 1 and 2.5 ppm represent 5 to 12% of the non-MEA protons. These protons are likely to be alkyl CH with moderate deshielding, consistent with the small alkyl amines and alkyl hydroxyl groups present in previously identified oxidative degradation and carbamate polymerization products. The terminal alkyl group of N-acetylethanolamine (2.0 ppm, oxidative degradation product) and some of the ring protons of N-(2-hydroxyethyl)succinimide (2.45 ppm, carbamate degradation product) were the only standards with resonance in this region. The strong linear relationship between the intensity of the terminal alkyl protons of N-acetylethanolamine and HSS is shown in Figure 12d. The number of unique ^{13}C nuclei with resonances between 15 and 35 ppm increased from six to twelve. The negative intensity of these six resonances in ^{13}C NMR DEPT experiments indicates that these nuclei have an odd number of protons attached and hence, are most likely to be terminal CH_3 groups of MEA degradation products.

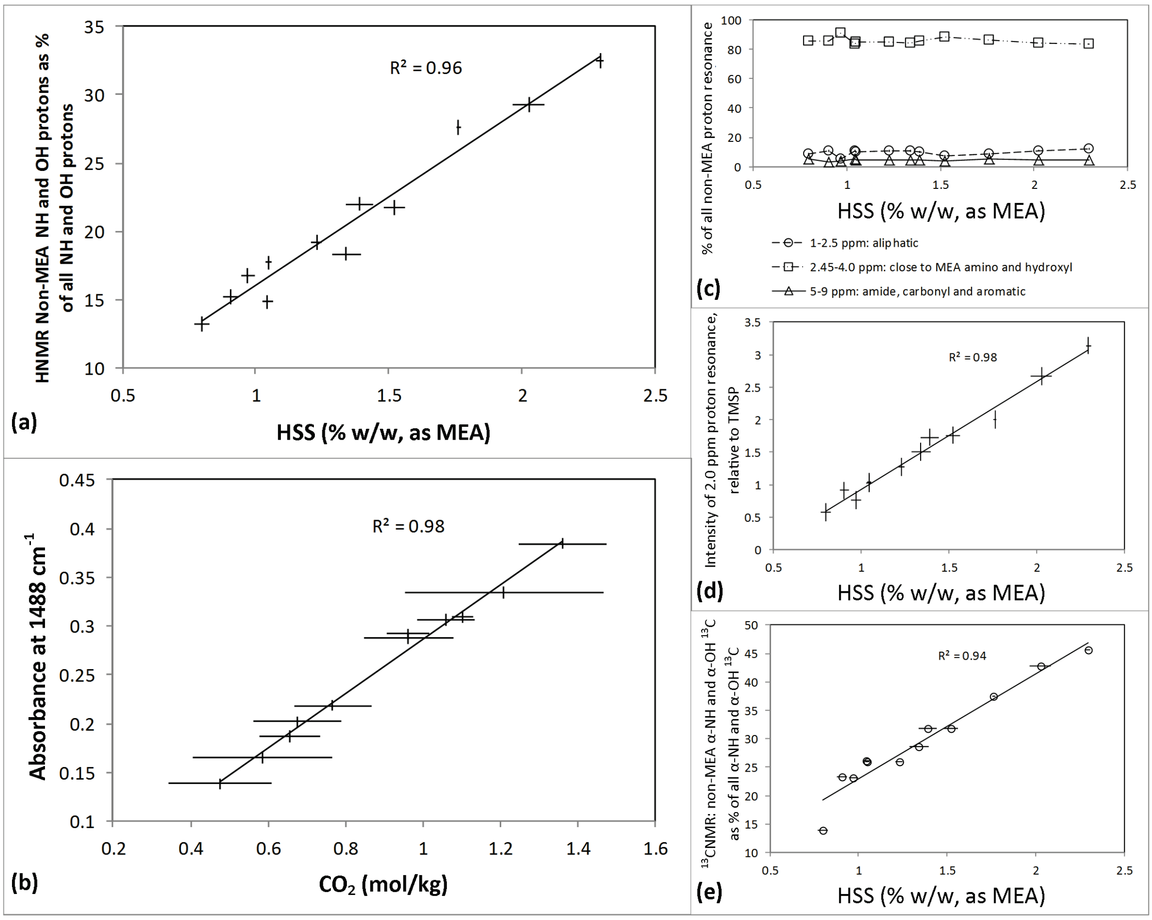


Figure 13. Correlations between ^{1}H and ^{13}C NMR, HSS and CO_2 concentrations

The integral of the complex unresolved resonances close to MEA and MEA carbamate α-amino and α-hydroxyl protons (between 2.45 and 4.02 ppm) increased during the sampling campaign Figure 13a shows the strong correlation with HSS concentration. This integral comprised 80 to 90% of all non-MEA protons, indicating that the α-amino and α-hydroxyl carbons are retained in the majority of MEA degradation products. This is consistent by proton resonances in this region for all of the standards analyzed. As the degradation increased, the number of unique ^{13}C nuclei resonances close to MEA and MEA carbamate α-amino and α-hydroxy resonances increased from approximately 20 to 50, suggesting an increase in the number of MEA degradation species.

Proton resonances between 5 and 9 ppm accounted for 3 to 5% of all non-MEA protons. The only standard compounds with resonances in this region was the aromatic N-(2-hydroxyethyl)imidazole). The number of unique carbon nuclei resonances between 160 to 185 ppm increased from 10 to 18, excluding carbamate resonances at 164.5 ppm. Except for the resonance at 170 ppm, DEPT intensities of these ^{13}C NMR resonances were negative, indicating these carbon nuclei are bonded to an odd number of protons. The small, broad proton resonances at 7.1, 7.25 and 7.75 ppm are likely to be amide N-H protons from oxidative degradation products.

4. DISCUSSION

4.1 Amine degradation

The impact of amine degradation on operational stability and energy efficiency of the PCC process was clearly demonstrated during this pilot plant campaign. As the amine absorbent condition deteriorated, the liquid to gas ratio (L/G) was decreased significantly in an effort to maintain stable operation of the pilot plant and minimise MEA loss. Decreasing the L/G ratio directly decreased both the CO_2 capture efficiency and energy efficiency of the PCC process. This highlights the importance of effective amine management in optimising energy efficiency.

In addition to increasing difficulties maintaining stable operation of the PCC pilot plant, amine degradation was evident from changes in the colour of the absorbent (from golden orange to reddish brown) and accumulation of HSS. This is consistent with observations of increasing color during laboratory scale degradation experiments (Bougie and Iliuta 2014). Over the campaign, approximately 0.16 kg HSS (as MEA) per t CO_2 captured was produced, which is similar to the 0.19 kg HSS per t CO_2 captured reported for the Esbjerg pilot plant (Knudsen, Jensen et al. 2009). However, the HSS concentrations (0.80 ± 0.03 to 2.29 ± 0.02% (w/w, as MEA) obtained in our study are higher than the 0.5 to 1.3% (w/w) reported by Knudsen et al (2009), but remained below the 3 % (w/w) reported by Wilson et al. (2004). The HSS concentrations we report are similar to the 0.09 and 0.19 eq/kg [equivalent to 0.5 and 1.2 % (w/w, as MEA)] HSS concentrations measured after laboratory-scale degradation by (Vevelstad et al., 2013). HSS is the standard method for measuring amine degradation and for this reason, the simularities between HSS concentrations reported by others and measured in these twelve samples from the pilot plant campaign indicates that the outcomes of this study are relevant to both laboratory and pilot-scale PCC processes.

The measurement of HSS at twelve regular intervals over the six month pilot-scale PCC campaign enabled a pseudo-first order reaction rate to be estimated. Figure 3 indicates that the HSS concentration doubled for every 10 t of CO_2 captured or 1% of the design capture capacity per year (1000 t CO_2/y). This is the equivalent to a doubling of HSS concentration every 3.65 days under full time capture operation. While this pilot plant was operated intermittently without corrosion inhibitors, oxidation inhibitors or amine reclaiming, this result highlights the importance of recent efforts to develop absorbents that are resistant to degradation, find effective oxidation inhibitors, and evaluate tools for monitoring amine degradation.

4.2 Structure of organic MEA degradation products

The changes in both organic degradation product concentrations (Figure 7) and ^1H NMR resonance (Figure 13a) indicate an increase from approximately 15% to 35% of the total organic carbon or α-amino and α-hydroxyl protons are associated with compounds other than MEA. This is consistent with the percent of total nitrogen (6-30%) present as compounds other than MEA after laboratory scale degradation trials previously reported (Vevelstad et al., 2014). However, HSS remained less than 2.3% (w/w, as MEA) which is less than 10% of the total MEA concentration. The consistent discrepancy between HSS concentrations and other measures of organic degradation products indicates that a significant portion of organic carbon other than MEA is neutral or cationic.

The ATR-IR difference spectra in Figure 8 indicate that the major changes in the organic compounds are associated with changes in the ratios of hydroxyl and amino groups and their hydrogen bonding environment, increases in carboxylate or amide groups, and decreases in carbamate groups. Both proton and carbon NMR indicate that the majority (80 to 90%) of the changes in the organic carbon influence the α-hydroxyl and α-amino shielding. This is consistent with the dominance of alkyl amino and alkyl hydroxyl groups in many commonly reported MEA degradation products (Gouedard et al., 2012).

Identification of N-acetylethanolamine terminal CH_3 protons at 2.01 ppm and the downfield shifts of α-amino and α-hydroxy protons in MEA degradation products are further evidence of the accumulation of oxidative degradation products in these samples. Three proton resonances between 5 and 9 ppm were identified as amide N-H protons by the magnitude of their shifts and quadrupole broadening due to the nitrogen. However, amide resonances were very small in the ^{13}C NMR spectra because there were few attached protons to contribute to the nuclear Overhauser effect (NOE).

4.3 Evaluating amine condition

HSS is the industry standard measure of amine degradation and many of the techniques investigated in this study correlated strongly with HSS. While HSS is a valuable measure of amine degradation, HSS is difficult to automate and therefore, poorly suited to on- or at-line monitoring because it is a laborious wet-chemical method. Some of the techniques considered in this study are more suitable for industrial applications because they are simple, rapid, readily automated and are linearly correlated to HSS measurements. Many of these techniques are also suitable for monitoring additional liquid streams such as amine reclaimer product and waste streams, lean flue gas water wash circuit, as well as aqueous waste streams that will need to be managed as part of an industrial PCC process.

The concentration of organic degradation products was measured by subtracting the MEA concentration from the TOC (total organic carbon) concentration. This included all organic degradation products with sufficient vapour pressure to accumulate in the aqueous amine absorbent but unlike HSS, excluded inorganic anions (e.g. SO_x, NO_x and chlorine from flue gas). Combining MEA measurements (using titration, GC-FID or another method) and TOC measurements would provide MEA concentration, CO_2 loading as well as a useful measure of amine degradation (organic degradation products). TOC and/or organic degradation products measurements would also be useful and applicable for monitoring the lean flue gas water-wash circuit, general waste streams as well as amine regeneration product and waste streams.

Absorbance of UV-Vis light between 250 and 350 nm is another suitable technique for on- or at-line monitoring of amine condition. The absorptivity of the amine absorbent samples at 270, 278, 305 and 313 nm (measured by UV-Vis) correlated very strongly with HSS throughout this pilot plant campaign. The locations of inflection point and maxima indicated that the heterocyclic aromatic oxidative degradation product N-(2-hydroxyethyl)imidazole was a significant contributor to absorbance. The broad and overlapping UV-Vis absorption bands were consistent with the complexity of the organic compounds in the degraded amine and the aqueous inter-molecular hydrogen bonding environment. Importantly, the wavelengths of UV absorption bands were not affected by increasing absorbent age or acidification, indicating that increasing concentrations of degradation products had more effect on the UV-Vis spectra than changing inter-molecular hydrogen bonding environments. This is a strong indication that monitoring changes in the absorbance at a limited number of wavelengths is likely to be sufficient, eliminating the need to monitor subtle changes in UV-Vis spectra and enabling the use of simpler, more robust filter photometers (Dickens, 2010). These observations indicate that absorptivity is an excellent candidate for monitoring amine absorbent condition because UV-Vis measurements are very simple, robust and readily installed in- or at-line.

More advanced spectroscopy techniques that are capable of distinguishing organic functional groups (such as ATR-IR and ^{1}H NMR) may be useful for more sophisticated monitoring of amine condition. The primary disadvantage of ^{13}C NMR was time required to obtain sufficient signal-to-noise, making it unsuitable for rapid monitoring the conditions amine absorbents. However, ^{13}C NMR provided valuable insight into the composition of the organic compounds present in these degraded amine samples.

Although the small changes in ATR-IR spectra were dominated by decreases in the CO_2 loading, increases in the absorbance of amides were evident. Other researchers have demonstrated that with suitable calibration, ATR-

IR is capable of providing MEA, carbamate, and carbonate concentrations in addition to amine degradation assessment (Einbu et al., 2012). However, using a simple spectral subtraction, the intensities of 1488 cm^{-1} may be a suitable indicator of CO_2 concentration while intensities at 1602 cm^{-1} and 1629 cm^{-1} are good predictors of HSS concentration in these pilot plant samples. This indicates that multivariate calibration and other spectral processing may be unnecessary for simply monitoring long-term degradation of amine absorbents during PCC. ATR-IR is robust and suited to on- or at-line applications and is likely to be useful for monitoring amine reclaimer product and waste streams. However, this technique is unlikely to provide useful information about samples with low organic content such as the lean flue gas water wash circuit.

Proton NMR was both the most expensive and the most informative technique investigated in this study. Proton NMR is rapid, robust and provides detailed information about individual degradation products (e.g. N-acetylethanolamine), different classes of degradation products (e.g. amides, aromatics and changes to the α-hydroxyl and α-amino groups) as well as CO_2 loading. With suitable selection of operating parameters and calibration, ^1H NMR may also be able to provide free MEA and MEA-carbamate concentrations. While NMR is likely to be too expensive for dedicated in- or at-line amine absorbent condition monitoring applications, it is likely to be a useful tool for developing a deeper understanding of amine degradation. In addition to the working absorbent, ^1H NMR is likely to be useful for monitoring amine reclaimer product and waste streams, the water wash circuit as well as the organic component of other waste streams.

5. CONCLUSIONS

Twelve samples of 30% (w/w) MEA absorbent were obtained during a six month pilot-scale PCC campaign, commencing with an absorbent that had been used for PCC for more than 700 h and concluding with samples containing sufficient amine degradation and/or impurities to impact the operation and CO_2 recovery of the PCC process. HSS concentrations (measured using cation exchange and acid-base titration) in the MEA samples used in this study are similar to previous pilot scale PCC amine degradation investigations. The concentration of organic degradation products (measured by acid-base titration and TOC) as well as ^1H NMR spectroscopy indicate that the organic carbon and protons present as compounds other than MEA (i.e. degradation products) increased from approximately 15% to 35% during the campaign. This is significantly higher than the estimate provided by HSS, indicating that a significant portion of the organic degradation products are neutral or cationic and therefore, not measured by HSS. The accumulation of amides from oxidative degradation was evident in both ATR-IR and ^1H NMR spectra.

TOC, UV-Vis and ATR-IR are all well established, inexpensive, rapid, reliable techniques and, unlike HSS measurements, are readily adapted to on- or at-line monitoring of MEA degradation during PCC. These techniques provided useful information about MEA degradation by measuring the (a) concentration of organic degradation products, (b) accumulation of the oxidative degradation product, HEI; and (c) changes in the infra-red absorption. In addition to monitoring absorbent condition, these techniques could also be used to monitor the accumulation of amine degradation products in other critical process streams including water-wash circuits, reclaimed amine, reclaimer waste and other aqueous waste streams. This would be of significant benefit to the next generation of PCC systems where on-going management of amine degradation and waste streams will be necessary to manage environmental issues.

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ABBREVIATIONS

ATR-IR, attenuated total reflectance – infra red spectroscopy; GC-FID, gas chromatography with flame ionization detection; HSS, heat-stable salts; MEA, monoethanolamine; NMR, nuclear magnetic resonance spectroscopy; PCC, post-combustion CO_2 capture; TOC, total organic carbon; UV-Vis, ultraviolet and visible light spectroscopy.

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Chapter 5: Accumulation of inorganics, metals and cations

Primary sources and accumulation rates of inorganic anions and dissolved metals in a MEA absorbent during PCC at a brown coal-fired power station

Chapter 5 contains a manuscript that has been submitted to the *International Journal of Greenhouse Gas Control* in 2015. The full reference for this publication is:

Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Chaffee, A., Meuleman, E., 2015. Primary sources and accumulation rates of inorganic anions and dissolved metals in a MEA absorbent during PCC at a brown coal-fired power station. International Journal of Greenhouse Gas Control, submitted.

This manuscript investigates the accumulation of inorganics, metals and cations in the MEA absorbent. The possible sources of these contaminants include the flue gas, fly ash, flue gas pre-treatment system and the make-up water added to the absorbent to maintain the water balance during the PCC campaign. Understanding the sources and concentrations of these contaminants is important because metals are known to catalyse oxidative degradation of aqueous amines but interactions between other contaminants have not yet been investigated. The accumulation of these inorganics, metals and cations is needed to enable aims A and B to be achieved.

Declaration for Thesis Chapter 5

Declaration by candidate

In the case of Chapter 5, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Defined the aims and scope of the manuscript, conducted all the laboratory work, wrote the initial draft of the paper and coordinated feedback and comments from all authors.	80

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
T. Vincent Verheyen	Provided valuable advice on the use and interpretation of data presented in this manuscript. Provided valuable advice on the structure, content and presentation of the manuscript.	N/A
Samuel B. Adeloju	Valuable advice on the structure, content and presentation of the manuscript. Co-ordinated submission and revision of the article	N/A
Erik Meuleman	Provided the sample set and associated pilot plant operation data. Provided valuable comments on the final drafts.	N/A
Alan L. Chaffee	Valuable input into final drafts	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature	A. Reynolds	**Date** 31-Mar-2015
Main Supervisor's Signature		**Date** 31/3/15

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

Primary sources and accumulation rates of inorganic anions and dissolved metals in a MEA absorbent during PCC at a brown coal-fired power station

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ABSTRACT

Post-combustion capture (PCC) of CO_2 from fossil fuel-fired power station flue gas is one of many technologies that are being developed to reduce anthropogenic greenhouse gas emissions in the medium term. Wet-gas scrubbing using aqueous amines is currently the most mature PCC technology suitable for separating CO_2 from coal-fired power station flue gases. In this study, a series of twelve samples of a degraded 30% (w/w) MEA absorbent were obtained over a six month pilot scale PCC campaign at a brown coal-fired power station in Australia. These samples were used to investigate the accumulation of heat-stable salts, inorganics and minerals. The heat-stable salts concentration increased from 0.80 to 2.29% (w/w, as MEA) and organic acids from the oxidative degradation of MEA were the largest component of heat-stable salts. Acid gases such as SO_x and NO_x, make-up water, ultra-fine fly-ash and corrosion were all sources of the minerals and inorganics that accumulated in the aqueous MEA absorbent. Corrosion was the single biggest contributor of transition metals and the abrupt change in ratios of Fe, Cr and Mo suggests that the dominant corrosion mechanism may have changed towards the end of the campaign. The rapid accumulation of minerals and inorganics during this PCC campaign highlights the importance of continuing research into the interactions between amine absorbents and inorganic or mineral contaminants. The data presented in this study are an important resource for design of laboratory scale experiments to investigate these physical and chemical interactions between aqueous amines, minerals and inorganics.

Keywords: post-combustion capture of CO_2, monoethanolamine, coal-fired power station, heat-stable salts, fly ash, pilot scale

Highlights:

- The accumulation of anions, cations and metals during pilot-scale PCC of CO_2 are measured
- Organic acids contribute more to heat-stable salts than inorganic anions
- Corrosion is a major source of dissolved metals
- Fly ash is a major source of cations

1. INTRODUCTION

Chemical absorption by aqueous amines is currently the most mature technology for post-combustion capture of CO_2 from coal-fired power stations. This technology has been used extensively for separating acid gases in a range of industries including natural gas processing and ammonia production (International Energy Agency, 2012). Managing the condition of the aqueous amine absorbent is important for reduction of the cost of capture, minimisation of corrosion, maximisation of operational stability and minimisation of environmental impacts of liquid and gaseous wastes.

Amine management guidelines published by Kohl and Nielsen (1997) for natural gas sweetening include regular monitoring of impurities; mechanical and activated carbon filtering; and amine reclaiming by distillation, ion exchange or dialysis. The US navy required the addition of N,N-diethanolglycine to minimise oxidative degradation of amines used to remove CO_2 from ambient air in submarines (Blachly and Ravner, 1966). However, these recommendations may not be sufficient to protect against the additional challenges presented by coal fired boiler flue gases such as: (a) significant oxygen concentrations (4-5%, Table 1); (b) strong acid gases such as SO_x and NO_x; (c) incomplete desorption of CO_2; and (d) potential for the accumulation of catalytic surfaces and dissolved metals from fly ash (Kittel et al., 2012).

Amine degradation is an active and important area of PCC research and has been reviewed recently and in detail by others (Gouedard et al., 2012; Vega et al., 2014). Oxidative degradation is the most rapid pathway and is particularly important because of the high oxygen content (4-5%, Table 1) of flue gases produced by combustion of fossil-fuels in excess air. In addition to decreasing the CO_2 capacity of the absorbent due to oxidative decomposition of amine molecules, many oxidative degradation products (e.g. organic acids) are stronger acids than carbonic acid and form heat-stable salts (HSS) with amines in the absorbent. Oxidative degradation is closely associated with corrosion of metal surfaces due to (a) the corrosiveness of oxidative degradation products and (b) the catalysis of oxidative degradation by dissolved transition metals (Goff and Rochelle, 2004; Léonard et al., 2014a; Vevelstad et al., 2014). Previous PCC pilot plants studies have reported the accumulation of up to 2.0% (w/w) oxidative degradation products in aqueous amine absorbents, demonstrating that managing oxidative degradation is an important consideration for optimising PCC (Moser et al., 2011).

Corrosion has been investigated at both the laboratory (Pearson et al., 2013; Wattanaphan et al., 2013) and pilot (Cousins et al., 2013) scales, indicating that corrosion is an important consideration for the operation of PCC plants at commercial scale. Key similarities and differences of the causes and management of corrosion during natural gas sweetening and PCC have been identified by Kittel et al. (2012). In addition to its close relationship with oxidative degradation, corrosion can lead to structural integrity issues and fouling. Despite efforts to minimise corrosion by using stainless steel piping, components and packing materials, iron concentrations of up to 450 mg/L have been measured in 30% MEA absorbents during pilot scale PCC of CO_2 from coal-fired power station flue gas (Mertens et al., 2013).

The typical gaseous composition of flue gas from Victorian brown coal-fired power stations is summarised in Table 1. Sulfur oxides (SO_x) are formed during coal combustion from oxidation of organic and inorganic sulfur in the coal. SO_2 is the dominant SO_x species and is highly soluble in aqueous solutions where it rapidly oxidises to sulfate in the presence of oxygen (Beyad et al., 2014; Miller, 2010). Sulfates rapidly form heat-stable salts (HSS) with aqueous amines, reducing the CO_2 capacity of the absorbent (Beyad et al., 2014). Due to the low sulfur content of Victorian brown coals and low population density surrounding brown coal-fired power stations in Victoria's Latrobe Valley (Australia), flue gas desulfurization (FGD) technologies are not installed (Allardice and Newell, 1991) and typical SO_2 concentrations range from 120-200 ppm (by volume, wet basis) (Artanto et al., 2012). In other countries, FGD typically reduces SO_x concentrations to 40-50 ppm (Notz et al., 2011) but due to the sensitivity of PCC systems to SO_x, dilute caustic scrubbers are usually installed upstream of CO_2 absorbers to reduce SO_x concentrations to <10 ppm (Wang et al., 2011).

Nitrogen oxides are formed from high temperature oxidation of both atmospheric nitrogen and organic nitrogen in the coal (Miller, 2010). The NO_x emissions from the brown coal-fired power stations in Victoria's Latrobe Valley (Australia) are also not controlled because of the (i) low nitrogen content (<0.6% dry, mineral matter and non-mineral inorganics free basis) of Victorian brown coals; (ii) relatively low combustion temperatures due to the high moisture content of the coal; and (iii) low population density surrounding the power stations (Allardice and Newell, 1991; George and Mackay, 1991). In other regions, NO_x emissions are typically reduced by controlling combustion conditions and/or post-combustion de-NO_x systems (International Energy Agency, 2012; Miller, 2010). More than 90% of NO_x in coal-fired power station flue gases is typically NO, with NO_2 and N_2O making up the balance (Artanto et al., 2012; Skalska et al., 2010). Unlike SO_2, NO has very low solubility in water (Skalska et al., 2010), resulting in very inefficient absorption of NO_x by amine absorbents. The potential for nitramine and nitrosamine formation by nitrosation of amines in the PCC absorbent by NO_x from the flue gas is a major concern for PCC systems but is not included in this study.

Table 1. Typical composition of flue gas from the brown coal fired power station at Loy Yang (Artanto et al., 2012)

Gas	**Concentration (wet basis)**
H_2O	20-23% (v/v)
CO_2	10-11% (v/v)
O_2	4-5% (v/v)
SO_2	120-200 ppm (v)
NO_x	150-250 ppm (v)

The chemical composition and mineralogy of fly ash in flue gas from coal combustion is highly variable and determined by the minerals and inorganics of the coal; combustion conditions; and post-combustion flue gas processing. The ash content of Victorian brown coals is very low in the Gippsland basin (Brockway and Higgins, 1991) and has been well characterised. The dominant minerals summarised in Table 2 are quartz, weathered clays (mostly kaolinite, $Al_2O_3.2SiO_2.2H_2O$) and aluminium hydroxide (AlOOH) with smaller amounts (<0.01%, dry basis) of potassium, titanium and iron minerals (Brockway et al., 1991; Kiss and King, 1977, 1979). Victorian brown coals also contain sodium, magnesium, calcium, iron and chloride inorganics associated with the organic coal structure and dissolved in the water phase (Brockway et al., 1991; Kiss and King, 1977, 1979). The formation of fly ash during and after combustion involves a wide range of reactions and interactions including:

vaporisation, oxidation and condensation of volatile inorganics; mineral dehydration and transformations; heterogeneous reactions between volatile inorganics and non-volatile minerals (e.g. formation of sodium silicates); and particle agglomeration (Brockway et al., 1991). Volatile minerals and trace elements are likely to be selectively concentrated onto ultra-fine fly ash particles because they represent the majority of the surface area (Brockway and Higgins, 1991; Xu et al., 2004). The composition of fly ash likely to reach the PCC process will also be impacted by ash deposition and separation by electrostatic precipitators or other particulate control systems.

Table 2. Typical composition of minerals and inorganics in coal from the Loy Yang mine (Brockway and Higgins, 1991)

Component	**Concentration (% w/w, dry basis)**
Ash	1.0
SiO_2	0.16
Al_2O_3	0.20
Ca	0.04
Mg	0.07
Na	0.14
Cl	0.18
Total S	0.31
Total Fe	0.04

Electrostatic precipitators are the only particulate control installed at the brown coal-fired power stations in the Latrobe Valley (Victoria, Australia) and they are typically operated with an efficiency of 95% (Allardice and Newell, 1991). In regions where more stringent particulate removal is required, higher particulate removal efficiencies are achieved using modern electrostatic precipitation technology or fabric filters (Miller, 2010). The caustic soda scrubbers typically installed upstream of PCC absorber trains to control NO_x and SO_x will also remove particulates but are not likely to remove sub—micron fly ash (Boot-Handford et al., 2014). Hence, ultra-fine fly ash particles are most likely to penetrate upstream particulate control measures and reach PCC absorbents.

Early research has demonstrated increased oxidative degradation of MEA in the presence of fly ash (Chandan et al., 2014; Silva et al., 2012), highlighting the importance of measuring the accumulation of fly ash in PCC absorbents. Calcium and potassium in the MEA absorbent at a PCC plant in Trona (CA) were attributed to fly ash (Strazisar et al., 2003). Very little additional information about the potential impact of dissolved and suspended minerals and inorganics on the degradation of aqueous amine absorbents is available in peer-reviewed literature. The accumulation of fly ash in aqueous amine absorbents is of interest because many of the minerals present in fly ash are likely to interact with amines due to their acidic and/or catalytic activity (Chandan et al., 2014; Silva et al., 2012). The ultra-fine fly ash particles that are most likely to by-pass particulate control measures are also likely to have a wide range of metals and inorganic elements that are volatile at peak coal-combustion temperatures adsorbed onto their surface (Nelson et al., 2010). These metals and inorganics are likely to dissolve into the aqueous amine absorbents where they are likely to either form HSS with aqueous amines or participate in catalytic oxidation (Silva et al., 2012).

Other minor sources of dissolved or particulate minerals and inorganics include post-combustion flue gas processing such as FGD and caustic scrubbers, make-up water and impurities in the amine as manufactured (Blachly and Ravner, 1966). Careful design of wet and dry scrubbing technologies such as FGD and caustic scrubbers is important for minimising entrainment and carry-over into the aqueous amine absorbents. Minerals and inorganics from make-up water are usually minimised by using demineralised or distilled water.

Accumulation of minerals and inorganics in absorbents during PCC of CO_2 from coal-fired power stations has been identified previously (Moser et al., 2011; Thompson et al., 2014) and laboratory degradation studies have considered the impact of acid gases and dissolved metal ions on amine degradation (Silva et al., 2012; Vevelstad et al., 2013). Early investigations into amine degradation and accumulation of minerals and inorganics at the pilot scale have focused on accumulation of metals and oxidative degradation (Moser et al., 2011).

This study builds on the early work by identifying and assessing the impact of the dominant sources of heat-stable salts and dissolved metals accumulated during pilot scale PCC from a Victorian brown coal-fired power station flue gas using a 30% (w/w) aqueous MEA absorbent. The concentrations of HSS, metals and inorganics are measured over a six month PCC campaign, providing important insights into the accumulation rates and probable sources of these impurities. The MEA absorbent had been used for PCC for more than 700 h prior to ensure the measured accumulation rates were not influenced by the use of new MEA. Both HSS and dissolved metals are important factors for amine degradation and for this reason, controlling the sources of these compounds will be crucial for commercial deployment of PCC. The information obtained in this study also helps to bridge the existing gap in available information about the potential impact of dissolved and suspended minerals and inorganics in aqueous amines. This information is also needed to enable the effects of coal-fired flue gas impurities on amine degradation to be determined and measured using laboratory scale experiments that closely mimic industrial conditions.

2. MATERIALS AND METHODS

2.1 Sample set

The twelve samples of 30% (w/w) MEA described in this study were obtained during a campaign at CSIRO's pilot plant at AGL's Loy Yang brown coal-fired power station as described previously (Reynolds et al., 2014). The sample lines were purged for 3-5 min prior to sampling to obtain a representative sample of the liquid absorbent. 30% (w/w) MEA was sampled directly into acid-washed high density polypropylene bottles. The samples were immediately transferred to a laboratory, subsampled for metals analysis and stored at -20°C in the dark. No settled solids were observed during storage and the samples were not filtered prior to acidification (for cation and metals analysis) or alkaline hydrolysis (for anion analysis). For this reason, the cation, anion and metal concentrations reported in this study include both dissolved and suspended colloidal analytes. The operation hours, tonnes of CO_2 captured, MEA concentrations and CO_2 loadings of these samples are given elsewhere (Reynolds, et al. 2015).

The pilot scale PCC campaign at CSIRO's PCC pilot plant at Loy Yang has been described in detail elsewhere (Reynolds et al., 2014; Reynolds et al., 2015) and details of a concurrent campaign are provided by Azzi et al. (2014). In summary, a batch of 30% (w/w) MEA (from Redox, Brisbane, Australia) was prepared and used to capture CO_2 at a PCC pilot plant operated by CSIRO for 640 hours at Tarong, Queensland Australia (Stanwell's 1400 MW black coal-fired power station) as part of investigations into PCC process modifications (Cousins et al., 2012) and corrosion (Cousins et al., 2013). The 30% (w/w) MEA was then stored for 18 months before being used to capture CO_2 at CSIRO's PCC pilot plant at Loy Yang, Victoria Australia (AGL's 2210 MW brown coal-fired power station) for a further 836 hours. During the PCC campaign at Loy Yang, approximately 200 L potable water was added to adjust the MEA concentration. No oxidation or corrosion inhibitors were added to the MEA and no amine reclaiming or filtering was conducted during the campaign. The flue gas was scrubbed with dilute sodium hydroxide upstream of the absorber train.

2.2 Heat-stable salts

Heat-stable salts were measured by cation exchange and acid-base titration as described by Reynolds et al. (in preparation). The moles of HSS (on an acid equivalent basis) were converted to a mass of MEA and expressed as % (w/w, as MEA).

2.3 Anions

Samples were analysed using a Dionex DX-120 ion chromatograph fitted with a 5µL loop, Dionex IonPac AG14A-5µm 3×30 mm guard column, AS14A-5µm 3 × 150 mm analytical column and Dionex ASRS Ultra II suppressor. The mobile phase was 4mM sodium carbonate (BDH Chemicals, >99% purity) and 0.5mM sodium hydrogen carbonate (BDH Chemicals, >99% purity) and the flow rate was 0.5 mL/min. 600 µL of 5N NaOH (Rowe Scientific, analytical reagent grade) was added to 500-550 mg of each sample and stored in the dark overnight to hydrolyse amides as described by (Sexton and Rochelle 2011). Prior to analysis, hydrolysed samples were diluted to 25.00 mL in mobile phase. To enable the direct comparisons between HSS and anion concentrations, the moles acid equivalents were calculated for each anion, converted to a mass of MEA and expressed as % (w/w, as MEA).

2.4 Metals and cations

Pre-weighed subsamples of the MEA absorbents were acidified with 1:1 HNO_3 (Analytical grade, Ajax Finechem and deionised water, MilliQ Academic, Millipore) and diluted to 100.0 mL with 1% HNO_3. Prior to analysis, samples were diluted a further 2:5 (v:v) in 1% HNO_3 and 2 mg/L scandium (internal standard, Australian Chemical Reagents, Australia) was added. Standards were prepared from a mixed metals and cations standard (#54704, Sigma Aldrich, Switzerland) in 1% HNO_3. Metals and cations were measured using a Varian Vista-Pro ICP-OES (Australia).

2.5 Statistical methods

All reported values are greater than the practical quantitation limits (PQL). PQLs were calculated as 15×SD×coverage factor where: SD is the standard deviation of seven replicates of 30% (w/w) MEA fortified with appropriate standards; and the coverage factor is 3.143, the Student's *t* value for six degrees of freedom of a one sided distribution with 99% confidence. Calibrations for anions, cations and metals were validated using NIST traceable control standards (catalogue numbers 697 (PotableWatR^{TM} Metals) and 981 (Ion Chromatography)) from ERA, Golden CO.

All analyses were conducted in triplicate and results are presented as the mean. Error bars and uncertainty intervals are one mean deviation (MD) of triplicate measurements. Monotonic trends were deemed significant (>99% confidence for 12 consecutive measurements) when the magnitude of the Kendall's τ value was greater than 0.667 (Esterby, 1996).

3. RESULTS AND DISCUSSION

3.1 Heat stable salts

Figure 1 and Table 3 show that the HSS concentrations increased from 0.80±0.03 to 2.29±0.01% (w/w, as MEA), but remained below the maximum concentration suggested by Kohl and Nielsen (1997) for aqueous amines used for sweetening of natural gas. Possible explanations for the increase in HSS concentration include: (a) the formation of HSS by amine degradation and accumulation of inorganic anions; and (b) the concentration of non-volatile anions as a result of evaporation of the amine.

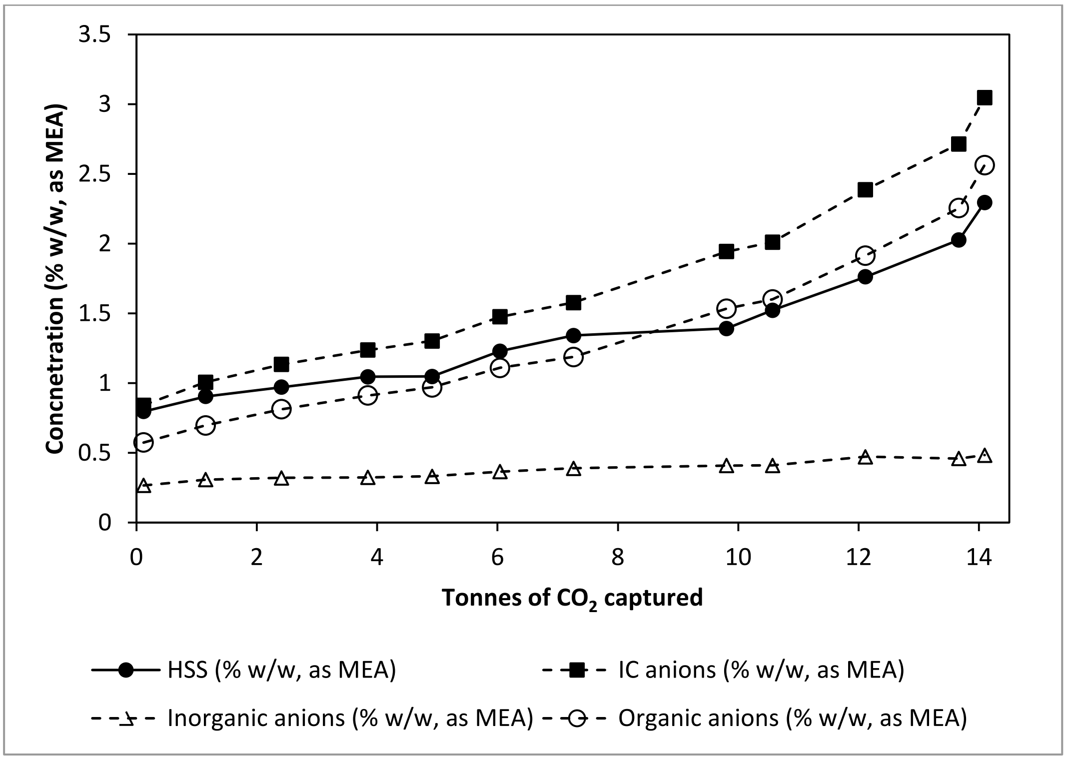

Figure 1. Accumulation of HSS, organic and inorganic anions in the MEA absorbent during the pilot scale PCC campaign at Loy Yang

Figures 1-3 show the changes in concentrations of inorganic and organic anions during this pilot plant campaign. On a mole of acid equivalent basis, the sum of the anions measured by ion chromatography accounted for between 105±3% and 135±2% of the total HSS measured by titration. In contrast, after laboratory-scale degradation in the absence of SO_x and NO_x, only 75 and 53% of HSS was accounted for by individual anions (Vevelstad et al., 2013), although it is unclear whether the anion concentrations were converted to acid equivalents. Interestingly, Figure 1 shows that the concentrations of organic anions increased more rapidly than the concentrations of inorganic anions. One unidentified anion detected by IC eluted between nitrate and sulfate and was excluded from Figure 1 because it could not be quantified.

Table 3. Comparison of HSS and anion concentrations in make-up water and the MEA absorbent with previously published guidelines and studies

Anion	**Make-up water (mg/L)§**	**30% (w/w) aqueous MEA absorbent**				
		Range§	**Units**	**Correlation coefficient (τ)^**	**Guidelines**	**Concentrations reported at other PCC facilities#**
Heat stable salts	NR	0.80(3) - 2.29(1)	% (w/w, as MEA)	1.000**	<3% (w/w, as MEA)[1] <10% of free amine[1]	0.5 and 1.2 % (w/w, as MEA)[5] 0.47% (w/w, as MEA)[4]
Chloride	12.7(9)	0.1017(1) – 0.167(1)	g/kg	0.909**		1600 ppm[3] 40 mg/L[4]
Nitrite	<2.3	0.107(3) – 0.108(3)	g/kg			130 ppm[3] <3 mg/L[4]
Nitrate	<2.2	0.60(2) – 1.51(2)	g/kg	0.970**		290 ppm[3] 720 mg/L[4]
Phosphate	0.0335(4)	<4	g/kg			
Sulfate	<2.2	1.49(2) – 2.40(7)	g/kg	0.879**	500 ppm[1]	2200 ppm[3] 3400 mg/L[4]
Formate	NR	2.09(3) – 11.8(1)	g/kg	0.788**	500 ppm[1]	0.2 % (w/w)[2] 799 mg/L[4]
Acetate	NR	2.10(6) – 5.10(6)	g/kg	1.000**	500 ppm[1]	1.8% (w/w)[2]
Oxalate	<9.3	0.52(1) – 3.1(2)	g/kg	1.000**	250 ppm[1]	

§The uncertainty intervals (calculated as one mean average deviation of triplicate measurements) of the smallest significant figure are given in brackets e.g. 12.7(9) = 12.7±0.9 mg/L. ^Kendall's τ relative to the tonnes of CO_2 captured at CSIRO's pilot plant at Loy Yang. #Only PCC facilities separating CO_2 from coal-combustion flue gas are included. *Non-parametric correlation is significant at the 0.05 level (2-tailed). **Non-parametric correlation is significant at the 0.01 level (2-tailed). NR, not reported. [1](Kohl and Nielsen, 1997); [2](Moser et al., 2011); [3](Strazisar et al., 2003); [4](Thompson et al., 2014); [5](Vevelstad et al., 2013).

Table 3 shows that phosphate (the only anion that was not detected in the MEA absorbent) was present at higher concentrations (33.6±0.4 mg/L) than other inorganic anions in the make-up water at the beginning of the pilot plant campaign. Approximately 200 L of make-up water was added to the MEA absorbent during the campaign, equating to approximately 45 mg/kg of phosphate in the absorbent at the end of the sampling campaign. The absence of detectable phosphate in the MEA absorbent indicates that either: (a) phosphate was removed from the MEA absorbent by interactions with other compounds and/or surfaces; or (b) non-volatile compounds were not significantly accumulated by evaporation during the pilot plant campaign and make-up water was not a significant source of inorganic anions or HSS.

The most rapidly increasing inorganic anion concentrations were sulfate (from 1.5±0.02 to 2.4±0.07 g/kg) and nitrate (from 0.60±0.02 to 1.5±0.02 g/kg). The final sulfate concentration exceeded the 500 ppm maximum concentration suggested by Kohl and Nielsen (1997) and was comparable to previously reported concentrations for PCC from coal-fired power stations using MEA absorbents (Strazisar et al., 2003; Thompson et al., 2014). The rapid accumulation and high concentrations of sulfate are consistent with the capture of CO_2 from flue gas containing SO_2.

At the beginning of this PCC campaign, the nitrate concentrations were more than three times higher than the nitrate concentrations reported by Strazisar et al. (2003) but comparable to the nitrate concentrations reported by Thompson et al. (2014). The two main sources of nitrate are oxidative amine degradation (Vevelstad et al., 2014) and NO_x from the flue gas. The slower accumulation of nitrogen oxides during PCC relative to the accumulation of sulfate is also consistent with previous observations (Strazisar et al., 2003; Thompson et al., 2014). However, even low concentrations of nitrogen oxides dissolved in aqueous amine absorbents are a concern for the formation of nitramines and nitrosamines (Fine et al., 2014; Vega et al., 2014).

The chloride concentration also increased during the pilot plant campaign but remained below the concentration reported by Strazisar et al. (2003). In the absence of reclamation, the concentrations of chloride in other PCC pilot plant absorbents were less than 100 mg/L (Aouini et al., 2014; Thompson et al., 2014). The wide variation in chloride contents of coals and incinerator feed-stocks is a possible explanation for the variable chloride concentrations measured in MEA absorbents at different PCC facilities. The most likely sources of chloride during the pilot plant campaign at Loy Yang were flue gas, ultra-fine fly ash and make-up water. The chloride concentration in the make-up water could not account for more than 10% of the final chloride concentration, and for this reason, flue gas and ultra-fine fly ash are most likely the main sources of chloride accumulated in the MEA absorbent.

The organic anions measured by ion chromatography (formate, acetate and oxalate) are products of oxidative degradation of MEA. Figures 1 and 2 show that these compounds are the major contributor to HSS and the concentrations in the amine absorbent rapidly increase during the pilot plant campaign. In contrast, organic anions were predicted to account for less than 25% of HSS accumulated in 30% MEA during PCC of CO_2 from an industrial incinerator (Aouini et al., 2014). This study indicated that the use of non-metal packing and construction material may be an effective strategy for minimising oxidative amine degradation (Aouini et al., 2014).

Table 3 shows concentrations of each organic anion exceeded the recommended maximum concentrations suggested by Kohl and Nielsen (2007) for natural gas sweetening. However, similar concentrations of acetate and formate have been measured previously in lean 30% MEA (w/w) during PCC of CO_2 from coal-fired power station flue gas (Moser et.al. 2011). The slightly lower formate concentration reported by Thompson et al. (2014) is consistent with their shorter time (100 h) of exposure to PCC conditions. These observations demonstrate that managing oxidative degradation is crucial for minimising accumulation of HSS during PCC from coal-fired power station flue gases. However, further discussion or investigation of oxidative degradation is beyond the scope of this work.

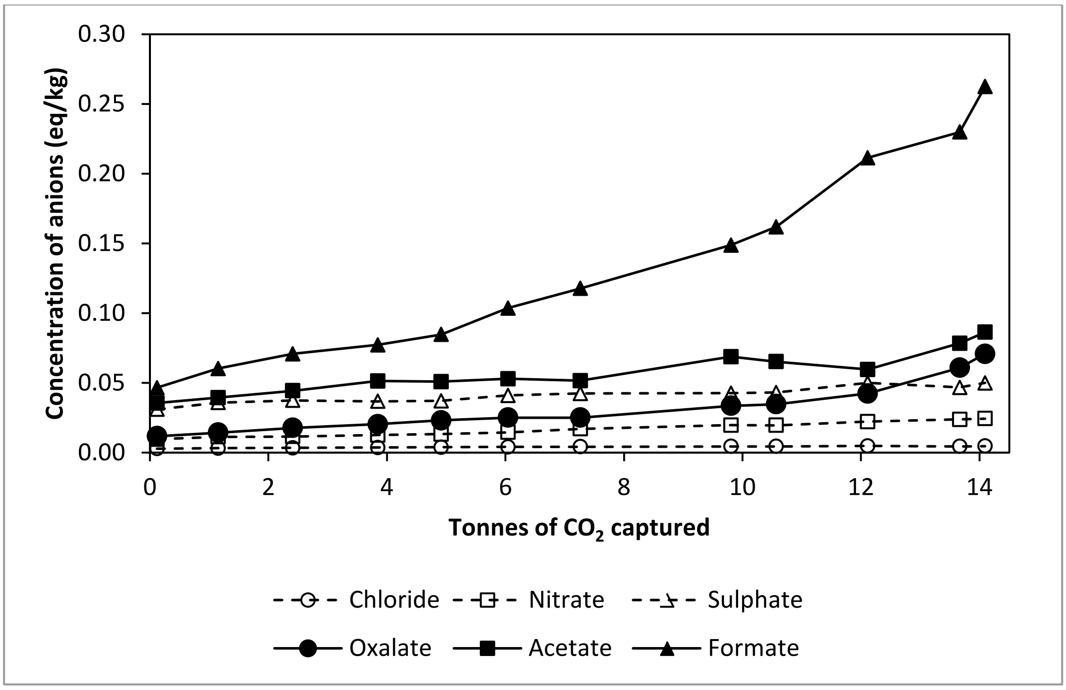

Figure 2. Accumulation of anions on an acid equivalent basis in the MEA absorbent during the pilot scale PCC campaign at Loy Yang
%RPD of triplicate measurements are all less than 10%.

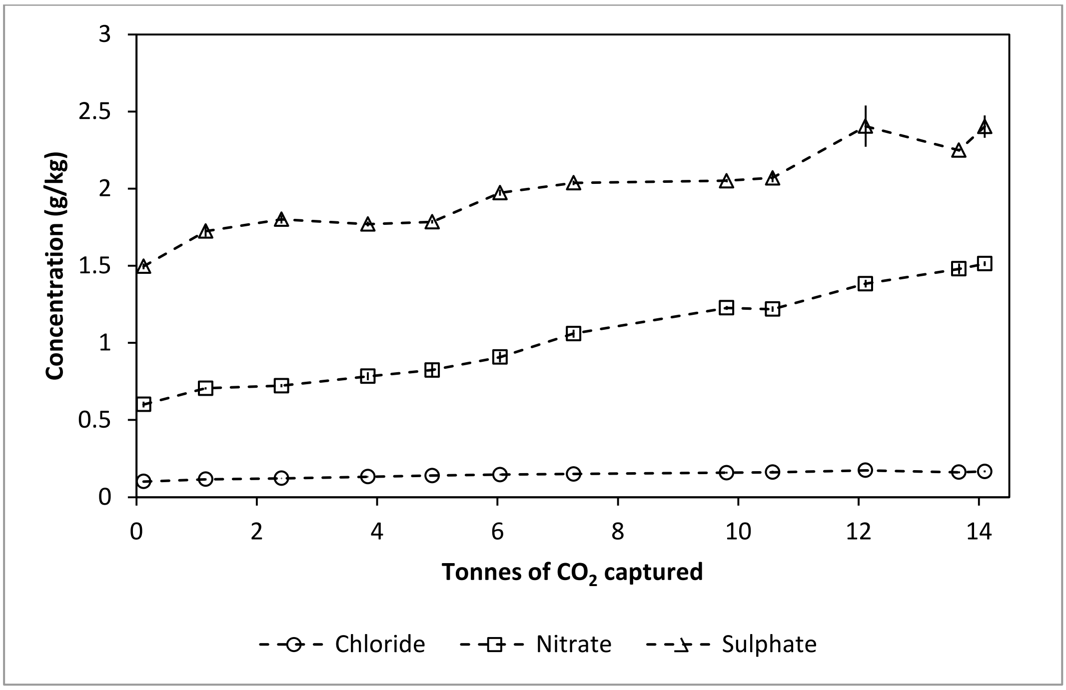

Figure 3. Concentrations of inorganic anions in the MEA absorbent during the pilot scale PCC campaign at Loy Yang
MD of triplicate measurements indicated by error bars

3.2 Cations

The concentrations of calcium, magnesium, potassium and sodium in the MEA absorbent increased during the PCC campaign (Figure 4). Table 4 shows that the concentrations of calcium and potassium during this PCC campaign were more than ten times the concentrations reported in a 30% MEA absorbent by Strazisar et al. (2003). The concentration of sodium was lower than the concentration reported by Strazisar et al. (2003) because alkaline salts such as sodium carbonate were not used to control HSS formation during this campaign.

The most likely sources of cations during the PCC campaign at Loy Yang are carry-over of entrained caustic soda from the flue gas pre-conditioning column; make-up water; and fly ash from the flue gas. The concentrations of cations and metals in the MEA absorbent, make-up water (at the beginning of the campaign) and caustic soda from the flue gas pre-conditioning column are summarised in Table 4.

At the beginning of the pilot plant campaign, the concentrations of all cations were lower in the make-up water than the 30% (w/w) MEA absorbent. Despite the addition of approximately 200 L, make-up water accounts for less than 60% of the increase in cation concentrations. The absence of a monotonic trend of the potassium concentration in the absorbent adds to the evidence that evaporation was not a significant cause of increasing concentrations of non-volatile compounds in the amine absorbent during this PCC campaign.

No significant positive monotonic trends were observed in the concentrations of calcium, magnesium and potassium in the caustic soda from the flue gas pre-conditioning column, which is consistent with the open loop operation of this system. Calcium and magnesium were present at lower concentrations in the caustic soda (i.e. flue gas pre-treatment scrubber) than the absorbent and the Ca/K and Ca/Mg ratios were between one-quarter and one-tenth of those measured in the absorbent.

These observations suggest that carry-over from the flue gas pre-treatment was not a significant source of contaminants because entrainment from the spray distributors at the top of the flue gas pre-conditioning column would contain cations in similar ratios to the bulk liquid. However, low levels of entrainment and carry-over may be significant sources of sodium in the absorbent because caustic soda (sodium hydroxide) is used to maintain the alkaline pH of the flue gas pre-conditioning scrubbing solution.

Table 4. Comparison of the concentrations of cations and metals in make-up water, caustic flue gas pre-conditioning absorbent, the MEA absorbent and previously published studies

	Make-up water	**Caustic absorbent from the preconditioning column**	**30% aqueous (w/w) MEA absorbent**		
	(mg/L)§	**Range (mg/L)§**	**Range (mg/kg)§**	**Correlation coefficient (τ)#**	**Concentrations reported at other PCC facilities**
CATIONS					
Ca	2.82(2)	0.58(2) - 1.83(2)	9.8(1) - 36.5(7)	0.992**	1.1 ppm[4]
K	1.10(1)	1.8(1) - 10.1(5)	4.5(2) - 10.2(4)	0.565*	2.2 ppm[4]
Mg	1.63 (1)	0.48(4) - 2.47(1)	2.4(3) - 6.2(2)	0.931**	
Na	7.7(2)	NR	17.5(1) – 62(2)	0.788**	80 ppm[4]
METALS					
Cr	<0.02	0.29(2) - 1.43(4)	1.18(1) - 4.20(7)	0.992**	5 ppm[1]
Cu	<0.06	<0.12	2.23(1) - 3.54(5)	-0.076	0.2 ppm[4]
Fe	<0.2	0.22(3) - 4.06(4)	14.1(3) – 199(1)	0.992**	1.4 ppm[4] ca. 15 – 30 ppm[3] ca. 10 – 450 ppm[2] 52 ppm[1]
Mn	<0.01	0.040(3) - 0.127(6)	0.48(6) - 2.12(4)	1.000**	2 ppm[1]
Mo	<0.03	0.22(5) - 2.31(2)	0.21(2) - 0.49(7)	0.970**	
Ni	<0.05	0.07(7) - 0.59(2)	2.2(4) - 4.6(1)	0.840**	6 ppm[1]
V	<0.02	<0.03	0.32(1) - 0.44(5)	0.260	
Zn	<0.2	<0.3	5.7(1) - 11.5(4)	0.870**	0.3 ppm[4]

§The uncertainty intervals (calculated as one mean average deviation of triplicate measurements) of the smallest significant figure are given in brackets e.g. 12.7(9) = 12.7±0.9 mg/L. ^Kendall's τ relative to the tonnes of CO_2 captured at CSIRO's pilot plant at Loy Yang. #Only PCC facilities separating CO_2 from coal-combustion flue gas are included. *Non-parametric correlation is significant at the 0.05 level (2-tailed). **Non-parametric correlation is significant at the 0.01 level (2-tailed). NR, not reported. [1](Léonard et al., 2014b); [2](Mertens et al., 2013); [3](Moser et al., 2011); [4](Strazisar et al., 2003).

Figure 5 shows the ratios of magnesium to calcium in the absorbent increased monotonically from approximately four to six. This is also consistent with the higher concentrations of magnesium than calcium in Victorian brown coal. Interestingly, there was no significant monotonic trend in the ratio of calcium to sodium and the ratio remained between one and two. This ratio is similar to the typical ratio of sodium to calcium in Victorian brown coal, suggesting that ash may be a more significant source of sodium than the caustic from the flue gas pre-conditioning column. The absence of a positive monotonic trend in the potassium concentration is consistent with the low potassium content of Victorian brown coal compared to calcium and magnesium. These observations suggest that penetration of fly ash through the pre-treatment column is likely to be the primary source of ash related cations in the MEA absorbent, particularly calcium, magnesium and potassium. Straziar et al. (2003) also attributed calcium and potassium in a 30% MEA absorbent to accumulation of fly ash, indicating that differing mineral and inorganic composition of the power station feed coal is likely to be the cause of the large discrepancies in the concentrations of these cations in the two 30% MEA absorbents.

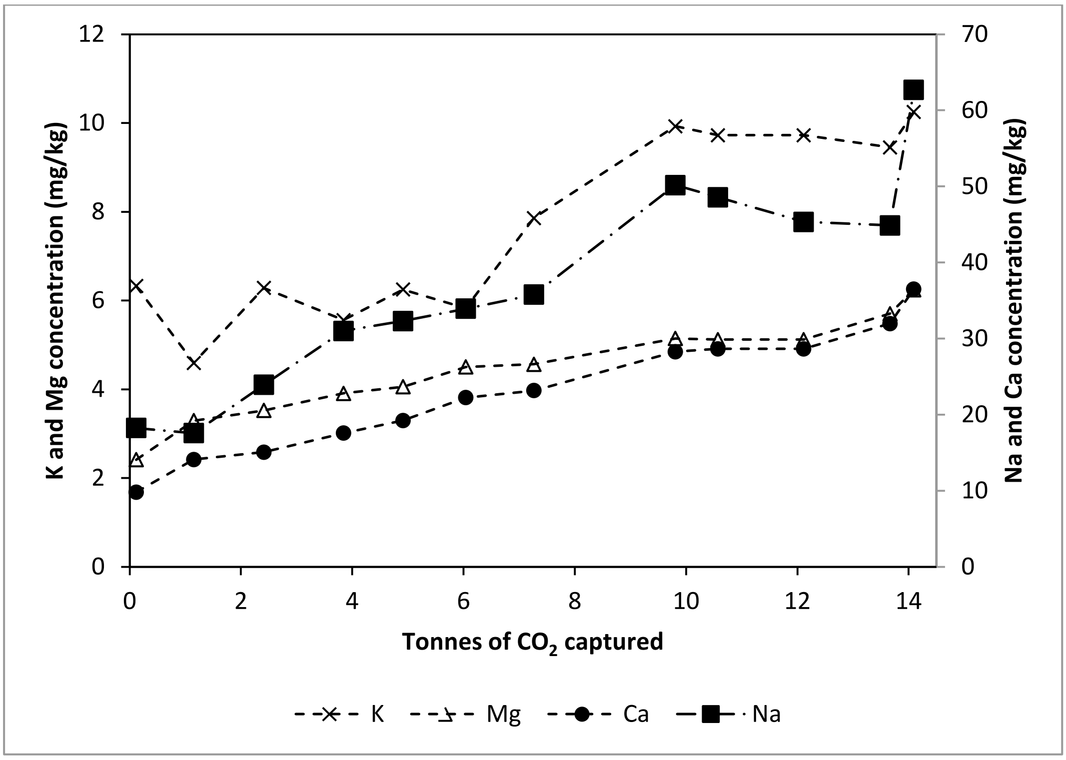

Figure 4. Concentrations of inorganic cations in the MEA absorbent during the pilot scale PCC campaign at Loy Yang

%RPD of triplicate measurements are less than 5%

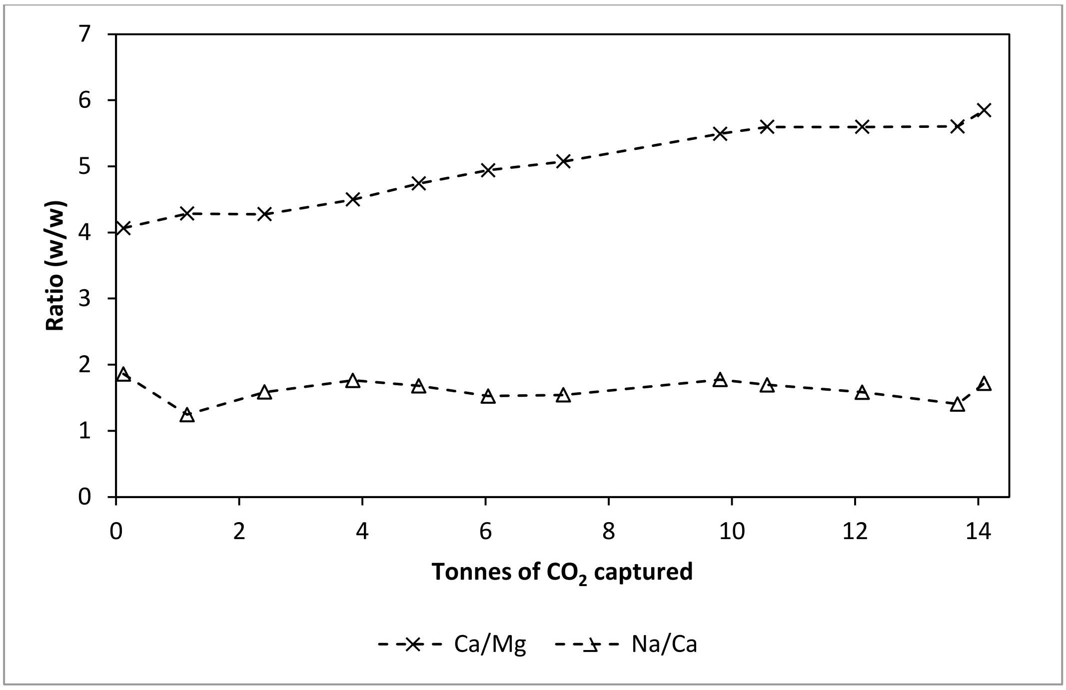

Figure 5. Ratios of inorganic cations in the MEA absorbent during the pilot scale PCC campaign at Loy Yang

3.3 Transition metals

The concentrations of transition metals in the MEA absorbent are shown in Figures 6 and 7. The solubilities of most transition metals in the aqueous amine are likely to be determined by competition between the low solubility of metal ions at high pH and formation of co-ordination complexes with the MEA and amine degradation products. Ample opportunity for precipitation and adsorption of metal ions is provided by the accumulation of ultra-fine fly ash, the large internal surface area of CSIRO's PCC pilot plant, the pall ring packing material and the stainless steel tubing of the sampling system. The metal concentrations reported in Table 4 and Figures 6 and 7 are the sum of dissolved and suspended metals that were present in the 30% (w/w) aqueous MEA absorbent.

Make-up water is unlikely to be a significant source of transition metals because they were not present at detectable concentrations (Table 4). Ultra-fine fly ash is also unlikely to be a significant source of transition metals because Table 2 indicates that the total iron concentrations in fly ash are typically similar to calcium concentrations, but the accumulation rate of iron in the MEA absorbent was significantly higher than the accumulation rate of calcium and other cations.

Table 4 and Figure 7 show that the concentrations of both copper and vanadium were well above the estimated practical quantitation limits (0.06 and 0.03 mg/kg respectively) in the MEA absorbent and the concentrations of these metals did not increase monotonically with the tonnes of CO_2 captured. This is consistent with the trends in phosphate and potassium concentrations discussed previously and provides firm evidence that the increases in the concentrations of transition metals were not caused by selective concentration of non-volatile components (i.e. due to evaporation of MEA) or solubility effects such as decreases in pH. This is in agreement with the findings of a related

PCC campaign at the same pilot plant (Azzi et al., 2014). However, corrosion of iron-based metal piping and packing material is likely to be a source of iron and other transition metals.

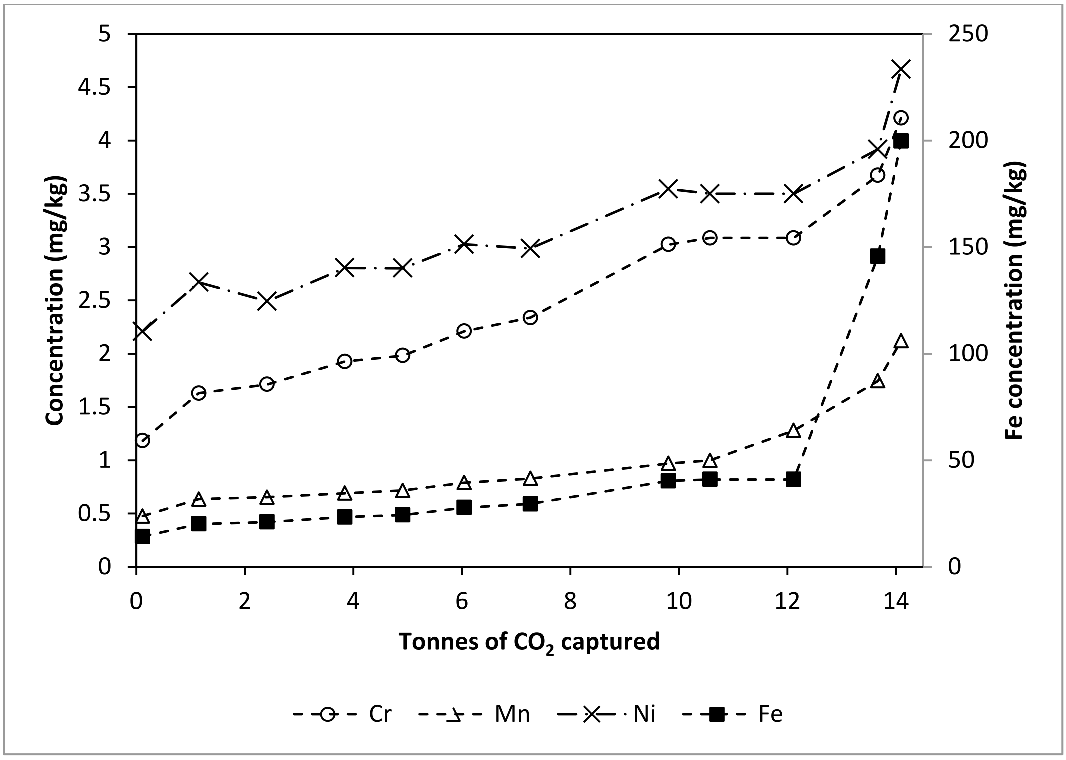

Figure 6. Concentrations of transition metals in the MEA absorbent during the pilot scale PCC campaign at Loy Yang.
%RPD of triplicate measurements are less than 5%

Figure 6 shows that iron was the most concentrated metal throughout the PCC campaign at Loy Yang and its concentration increased from 14±0.3 mg/kg to 199±1 mg/kg. Other metals present at trace amounts in 316 and 304 stainless steels (e.g. chromium and molybdenum) were present at significantly lower concentrations than iron, suggesting that corrosion is a possible source of these transition metals. Unlike these other metals, the concentrations of iron were significantly higher in the last two samples than the earlier samples obtained during this pilot plant campaign. Table 4 shows that the final iron concentration was significantly higher than the concentration in MEA during one pilot plant campaign (Moser et al., 2011) and lower than the highest concentration reported by Mertens et al. (2012). The wide variation in reported iron concentrations is consistent with corrosion being the main source of iron because the rate of corrosion will be dependent on the history of the pilot plant. The 14.2 to 199 mg/kg of iron measured during this PCC campaign is equivalent to 0.23 to 3.6 mmol/kg which is similar to the iron concentrations (0.003-4 mM) in laboratory scale catalytic degradation studies conducted by Chi and Rochelle (2002), but higher than the <0.14 mM studied by Goff et al. (2004). For these reasons, the primary source of transition metals, such as iron, manganese, chromium, nickel, molybdenum and vanadium in the aqueous MEA absorbent is likely to be corrosion of metal surfaces including piping, pumps, heat exchangers, instruments and packing material.

The majority of the metallic surface area exposed to the amine absorbent is the column packing of the absorber and desorber trains (both 316 stainless steel, 16 mm pall rings). The piping material downstream of the flue gas pre-conditioning column is 304 stainless steel. However, corrosion of 316 stainless steel vessels has been observed during laboratory scale degradation of MEA (Bougie and Iliuta, 2014). The bulk elemental composition specifications for 304 and 316 stainless steels from American Society of Metals (ASM) are listed in Table 5.

The increasing concentrations of chromium, manganese and nickel in Table 4 and Figure 6 provide strong evidence that corrosion of stainless steel surfaces is a significant source of these metals. Molybdenum is added to 316 grade stainless steel, but not to 304 grade stainless steel, and for this reason, the presence and increase in concentrations of molybdenum in Figure 7 suggests that corrosion of 316 stainless steel was a significant contributor of transition metals in the absorbents. This is consistent with the large 316 surface area of the pall ring packing material and evidence of corrosion of packing material in the desorber shown in Figure 8.

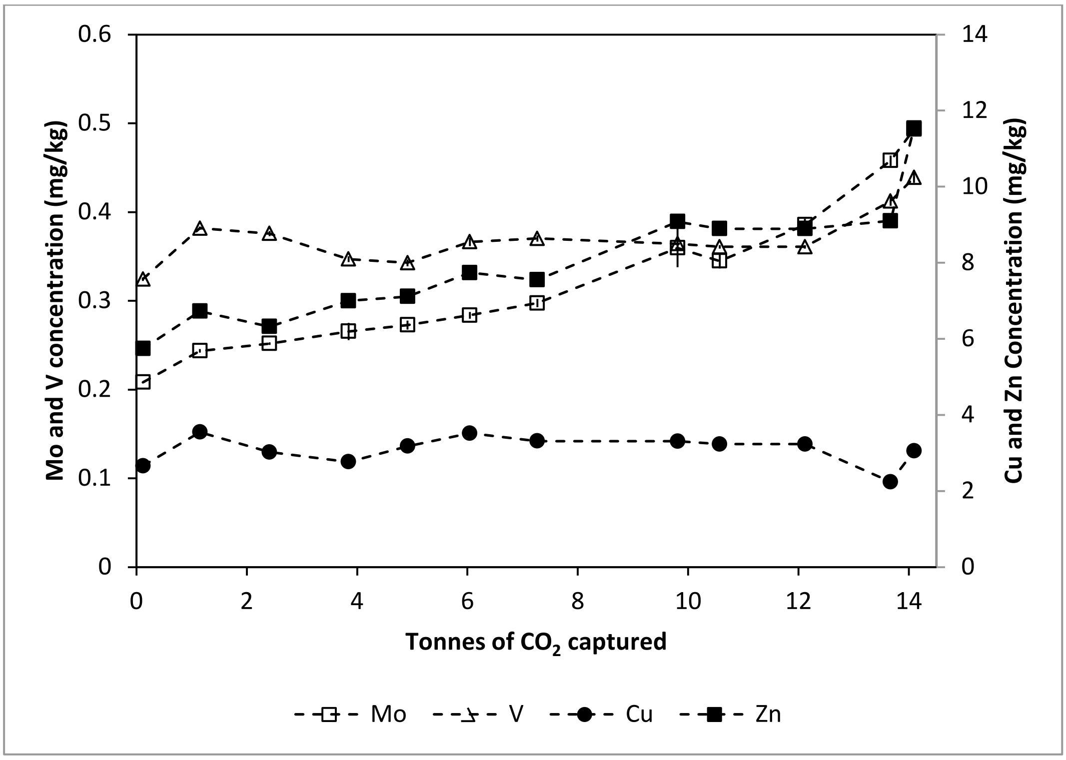

Figure 7. Concentrations of trace level transition metals in the MEA absorbent during the pilot scale PCC campaign at Loy Yang. Error bars are the MD of triplicate measurements.

Table 5. Composition of 304 and 316 stainless steels specified by ASM (ASM International Handbook Committee, 1990)

	Concentration (%, min)	
Element	**304 Stainless steel**	**316 Stainless steel**
Fe*	66-71	62-69
C	0.08	0.08
Mn	2.00	2.00
Si	1.00	1.00
Cr	18-20.0	16-18.0
Ni	8-10.5	10-14.0
Mo	Not specified	2-3.0
P	0.045	0.045
S	0.03	0.03

*calculated by difference.

3.4 Corrosion

The severe corrosion of the pall rings from the desorber shown in Figure 8 is the result of CO_2 capture using a wide variety of aqueous amine absorbents at CSIRO’s PCC pilot plant and cannot be attributed solely to the current campaign. Previous corrosion of the metal surfaces may also be a significant contributing factor to the rapid increase of transition metal concentrations in the absorbent measures during this PCC campaign. Even so, the packing material in Figure 8 has only been used for a fraction of the continuous operating hours that will be required for commercial-scale PCC of CO_2 from coal-fired power stations. This observation strongly indicates that corrosion management should be a major consideration for design and operation PCC.

Figure 8. Photo of pall rings sampled from the absorber (top) and desorber (bottom) after the PCC campaign at Loy Yang

A change in corrosion mechanism may be indicated by the large difference in the ratio of iron to chromium ratio between the first ten samples and the last two samples (Figure 9). The ratio of chromium and manganese concentrations increased until approximately 10 t CO_2 was captured and then decreased. The concentrations of chromium, manganese and nickel increased monotonically throughout the pilot PCC campaign, however, after the capture of 10 t of CO_2, the manganese concentration increased more rapidly than the chromium. However, the chromium/nickel ratio consistently decreased while the chromium/manganese ratio consistently increased. Interestingly, the rate of change of the chromium/manganese ratio increased abruptly after 10 t CO_2 was captured. Both nickel and manganese are added to stainless steels to maintain the austenitic structure and promote the formation of the chromium oxide layer (ASM International Handbook Committee, 1990). The increasing concentrations of these metals could indicate that uniform chromium oxide passive layers were not maintained and the underlying metal may have been corroding. This possible depletion of the chromium on the surface of the stainless steel, leading to loss of the chromium oxide passivation layer and rapid corrosion warrants further investigation.

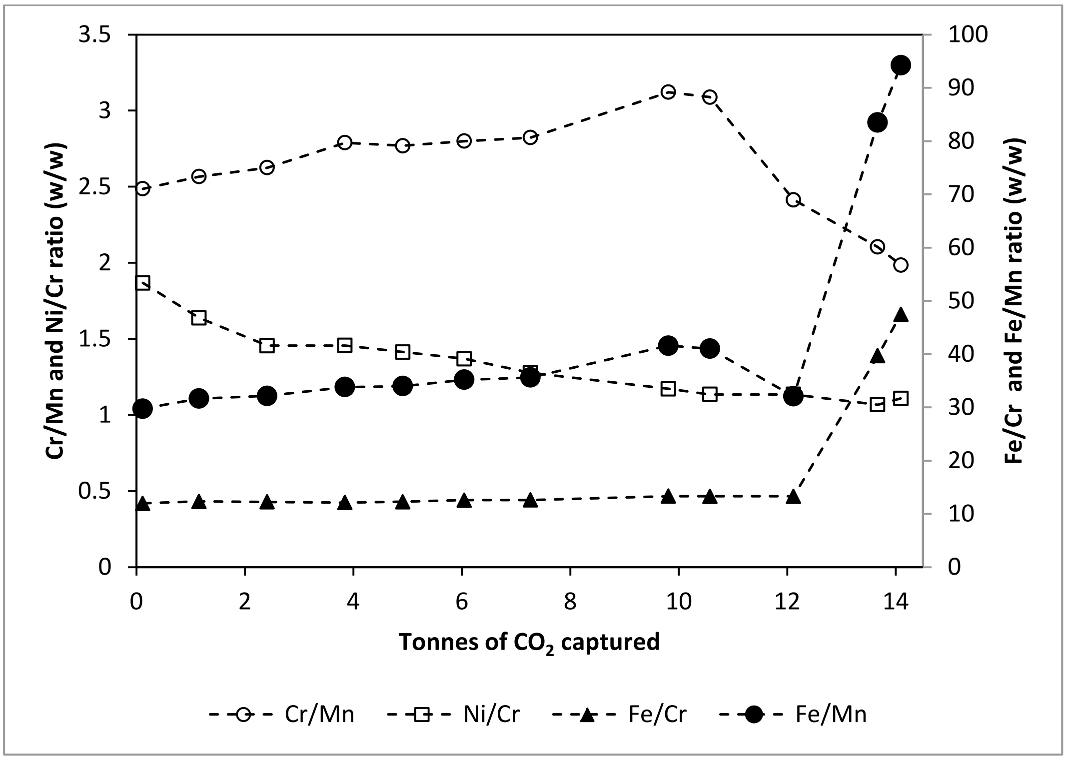

Figure 9. Ratios of transition metal concentrations in the MEA absorbent during the pilot scale PCC campaign at Loy Yang

4. CONCLUSIONS AND RECOMMENDATIONS

This study reports the changes in concentrations of inorganic anions, cations and transition metals in a 30% (w/w) aqueous MEA absorbent during pilot scale PCC at a Victorian brown coal-fired power station. The severe degradation of the MEA absorbent was evident from the dark red-brown colour and the HSS concentrations ranged from 0.80 ± 0.03 to 2.29±0.01% (w/w, as MEA). The data presented in this study are representative of inorganics and metals that are likely to accumulate during larger scale PCC operations and, for this reason, the data will be a valuable reference for the design of experiments to investigate individual aspects of amine degradation at the laboratory scale.

Inorganic anions were minor contributors to HSS compared to organic anions, highlighting the importance of managing oxidative degradation during PCC. Concentrations of sulfate and organic anions exceeded the maximum recommended concentrations for treating natural gas. The concentrations of chloride, nitrate and sulfate were comparable to concentrations previously reported during PCC of CO_2 from coal-fired flue gas using 30% MEA and coal-fired flue gas was the most significant source of these anions.

Make-up water and penetration of ultra-fine ash were more significant sources of inorganic cations (sodium, calcium, magnesium and potassium) than entrainment of dilute caustic soda used to remove strong acid gases (primarily SO_x and NO_2) from the flue gas. The composition of fly ash varies widely between different coal seams and combustion conditions and, for this reason, there is a wide variation in the concentrations of these cations measured in amine absorbents at different PCC plants. However, further work is needed to determine if the accumulation of ultra-fine fly ash during PCC is likely to result in heterogeneous interactions between aqueous amine absorbents and the potentially catalytic surfaces of fly ash minerals (such as clays, silicate and aluminium oxides).

Severe corrosion of 316 stainless steel packing material in the desorber was the dominant source of iron and other transition metals. Iron concentrations of up to 199±1 mg/kg were measured in the MEA absorbent, which is significantly higher than some concentrations reported previously for PCC using 30% MEA without corrosion inhibitors (Moser et al., 2011; Strazisar et al., 2003) but lower than the maximum concentration reported during another PCC campaign (Mertens et al., 2013). Both zinc and copper were present at higher concentrations than reported by Strazisar et al. (2003). Evidence for such high concentrations of metal ions in amine absorbents suggests that research into corrosion should consider limiting catalytic oxidative amine degradation in addition to ensuring structural integrity. The possibility of chromium depletion at the surface stainless steel structures and packing material also warrants further investigation into corrosion mechanisms.

The solubility of many transition metals is limited in aqueous alkaline solutions and although the solubility of iron and other transition metals is likely to be increased by the formation of co-ordination complexes in aqueous amine absorbents, the possibility of metal precipitation and/or adsorption onto other surfaces should be considered. Dissolved metal ions and metal atoms adsorbed onto ultra-fine fly ash particles or other surfaces may result in different rates and mechanisms of catalytic oxidative degradation of amines. For this reason, further work is needed to: (a) distinguish transition metals present as dissolved ions from transition metals adsorbed onto other surfaces or present as precipitates; and (b) determine the solubilities of common transition metals in aqueous amines under typical PCC conditions.

Overall, these results demonstrate that acid gases (such as SO_x and NO_x) make-up water, ultra-fine fly ash and corrosion are all potential sources of minerals, inorganic compounds and metal ions in amine absorbents. This highlights the importance of on-going research into the interactions between aqueous amines and acid gases (such as SO_x and NO_x), metal surfaces, and dissolved or suspended metals. Understanding potentially catalytic interactions between common fly ash minerals (such as clays, silicate and aluminium oxides) will also require a more comprehensive knowledge of the characteristics of ultra-fine fly ash. However, unlike acid gases and corrosion products, the characteristics of ultra-fine fly ash will depend on the coal and combustion conditions at each power station. The importance of considering dissolved and suspended metal concentrations in the absorbent, in addition to structural integrity, when determining corrosion rate guidelines is also emphasised.

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ABBREVIATIONS

FGD; flue gas desulfurization; HSS, heat-stable salts; MEA, monoethanolamine; IC, ion chromatography; ICP-OES, Inductively coupled plasma with optical emission spectroscopy detection; PCC, post-combustion CO_2 capture.

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Chapter 6: GC-MS method development

Comparison of sample preparation methods for the GC-MS analysis of monoethanolamine (MEA) degradation products generated during post-combustion capture of CO_2

Chapter 6 contains a manuscript that has been submitted to the *Energy and Fuels* journal in 2015 for peer review and publication. The full citation for this paper is:

Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Chaffee, A., Meuleman, E., 2015. Comparison of sample preparation methods for the GC-MS analysis of monoethanolamine (MEA) degradation products generated during post-combustion capture of CO_2. Energy and Fuels, submitted.

The cation exchange method described in this chapter was used for chapter 7 and enabled all three aims of this thesis to be achieved. The method described in this paper is complementary to HPLC methods used by other research groups to measure amine degradation products and is an important contribution to PCC research because methods for measuring amine degradation products are needed to: (a) investigate amine degradation during pilot scale PCC and (b) investigate the potential impacts of PCC and amine degradation on human health and the environment.

Declaration for Thesis Chapter 6

Declaration by candidate

In the case of Chapter 6, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Defined the aims and scope of the manuscript, conducted all the laboratory work, wrote the initial draft of the paper and coordinated feedback and comments from all authors.	80

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
T. Vincent Verheyen	Provided valuable advice on the use and interpretation of data presented in this manuscript. Provided valuable advice on the structure, content and presentation of the manuscript.	N/A
Samuel B. Adeloju	Valuable advice on the structure, content and presentation of the manuscript. Co-ordinated submission and revision of the article	N/A
Erik Meuleman	Provided the sample set and associated pilot plant operation data. Provided valuable comments on the final drafts.	N/A
Alan L. Chaffee	Valuable input into final drafts	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature	A. Reynolds	**Date** 31-Mar-2015

Main Supervisor's Signature		**Date** 31/3/15

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

Comparison of sample preparation methods for the GC-MS analysis of monoethanolamine (MEA) degradation products generated during post-combustion capture of CO_2

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ABSTRACT

As the development of chemical absorption technology for post-combustion capture (PCC) of CO_2 from coal-fired power station flue gases proceeds towards commercial deployment, the focus on establishing a thorough understanding of the degradation of the aqueous amine absorbents is increasing. However, there is a need to develop and demonstrate robust analytical methods that are capable of measuring the concentrations of amine degradation products in aqueous monoethanolamine (MEA) matrix during pilot-scale PCC. In this study, sample cleanup and derivatisation methods that enable reliable and robust analysis of MEA degradation products by GC-MS are described. These methods are validated for samples of a severely degraded 30% MEA (w/w) absorbent that were obtained during a six month campaign at CSIRO's PCC pilot plant at a coal-fired power station in Victoria, Australia.

Two sample cleanup methods were evaluated: dehydration (by rotary evaporation and molecular sieves) and cation exchange. Both of these methods separated the water from the absorbent, enabling the use of water sensitive derivatisation reagents (BF_3:n-butanol and acetic anhydride). Both derivatisation and sample cleanup were necessary components of the GC-MS analysis of these analytes in the degraded 30% (w/w) MEA samples.

The cation exchange sample preparation method was preferred for the analysis of organic degradation products in these samples because the recovery and repeatability of GC-MS measurements following cation exchange were superior to the GC-MS measurements following dehydration. The cation exchange method provided fewer opportunities for continued amine degradation during subsequent analysis steps because it (a) separated acidic analytes from basic analytes and (b) removed some inorganic interferences. The sensitivity, repeatability and accuracy of this GC-MS analytical method could be improved by: (a) increasing the scale of the cation exchange and/or derivatisation procedures; (b) optimizing the derivatisation reaction condition; and (c) the use of a narrower bore (e.g. 0.25 mmID) GC-MS column. The proposed cation exchange and derivatisation procedures can be readily adopted for the quantification of organic degradation products in other aqueous amine absorbents, providing important insights into the degradation of amine absorbents during PCC of CO_2.

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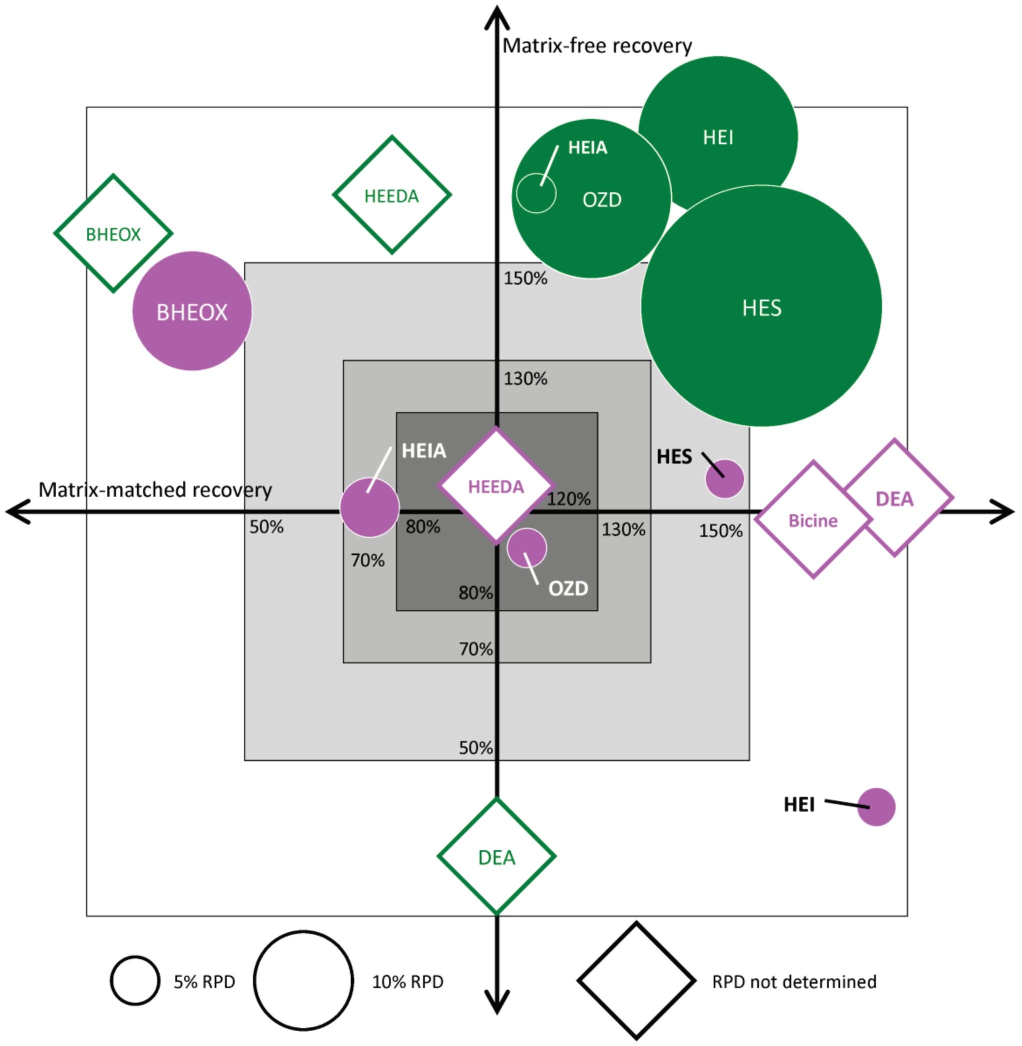
Graphical abstract



Green, dehydration; purple, ion exchange; BHEOX, N,N-bis(2-hydroxyethyl)oxamide; DEA, diethanolamine; HEEDA, N-(2-hydroxyethyl)hydroxyethylamine; HEI, N-(2-hydroxyethyl)imidazole; HEIA, N-(2-hydroxethyl)imidazolidione; HES, 2-hydroxyethylsuccinimide; OZD, 2-oxazolidione; RPD, relative percent difference.

Keywords: solid phase extraction, SPE, cation exchange, SCX, derivatisation, acetylation, degradation

1. INTRODUCTION

Post-combustion capture (PCC) of CO_2 remains an important component of many strategies proposed for the management of global atmospheric CO_2 emissions in the medium-term.[1,2] Wet gas scrubbing with aqueous amine systems is currently the most advanced technology for separating CO_2 from fossil fuel-fired power station flue gases.[1] One important aspect of recent research into the adaption of this technology for PCC of CO_2 is the chemical degradation of aqueous amine absorbents.[3] A wide range of aqueous amine systems are being used or developed for PCC of CO_2 but degradation of MEA (2-aminoethanol) has been studied most comprehensively.[3,4] MEA and many of its degradation products are thermally labile below 300°C, contain multiple polar functional groups, are alkaline and, hence, reactive to acids.[4] During PCC of CO_2, aqueous amine systems accumulate impurities from chemical degradation; contact with metal surfaces; and flue gases containing SO_x, NO_x, oxygen and fly-ash.[5,6] There is, therefore, an urgent need for the development and demonstration of analytical methods that enable the reliable identification and quantification of organic degradation products in aqueous amine systems.

Both GC-MS and HPLC-MS have been used extensively for the identification and quantification of semi-volatile organic compounds (SVOCs) produced during the degradation of aqueous MEA.[7] Many of the identities of these SVOCs have been independently verified by multiple techniques (e.g. GC-MS, HPLC-MS, GC-FTIR) or by the analysis of pure standards, although the structures of a few organic degradation products remain uncertain.[4,7-9] Recently, a HPLC-MS method for the quantification organic degradation products in degraded aqueous amine absorbents has been published.[10] However, despite the use of GC-MS for identification and quantification of organic degradation products in aqueous amines, no detailed GC-MS method validation data is available in the peer-reviewed literature.

The accumulation of non-volatile minerals and inorganics in amine absorbents during PCC[5,6,11] and the strong likelihood that these impurities will interfere with reliable GC-MS analyses suggests that a sample cleanup step will be necessary. The use of suitable sample cleanup procedures could resolve the issues identified with use of DAI GC-MS (direct aqueous injection with gas chromatography mass spectrometry) for the quantification of SVOCs in degraded 30% (w/w) aqueous amine absorbents.[23] Well established sample cleanup and preparation methods, including liquid or solid phase extraction and derivatisation, are used extensively for the reliable GC-MS quantification of challenging analytes in biological and environmental matrices.[12-14] The adaption and use of these sample preparation and/or derivatisation methods for the analysis of SVOCs in the aqueous MEA absorbents has not been reported in peer-reviewed literature and is likely to enable the use of GC-MS for reliable quantification of VOCs in aqueous amine absorbents because these matrices have similar characteristics.

The characteristics of typical aqueous amine systems used for PCC of CO_2 present a number of well documented challenges for GC analysis including: (a) high alkalinity; (b) high concentrations (10-70%) of water and amine(s); (c) both acidic and basic analytes; (d) strongly polar and strongly hydrophilic analytes;[12, 15] (e) thermally labile analytes;[12,13,16] and (f) presence of non-volatile anions and cations.[12] Analysis of alkaline samples and/or analytes are often complicated by interactions with exposed silanols in GC inlet or injector liners and column materials.[12] Non-volatile salts as well as organic acids and bases are also likely to interact with each other and deposit in the injector liners.[12] Many of these interactions are known to cause poor and deteriorating peak shapes[12,13,17] as well as variable matrix-induced enhanced response[12,13,16,17] during GC analysis.

Matrix-induced enhancement of GC response is a significant issue for the analysis of pesticides,[12-14] biological molecules and drugs.[15] The artificial increase in analyte response due to matrix-induced enhancement is commonly reported as either a percentage or ratio of the analyte response in (a) the clean analytical solvent compared to (b) the sample matrix.[12,14,15,17] The causes and remedies of matrix-induced enhanced GC response have been critically reviewed elsewhere.[12,13] The susceptibility of polar, thermally labile and compounds with strong hydrogen bonding capacity to matrix-induced enhanced GC response has been well established.[12,15] Matrix-induced response enhancement can be minimized or stabilized by: (a) optimizing injection conditions to reduce interactions between the analytes and surfaces of the GC-MS system;[12,16,17] (b) derivatisation;[15] (c) the use of matrix-matched calibration standards;[12,16,17] and (d) the separation of components of the matrix and the analytes prior to analysis.[12,16] For these reasons, the use of sample cleanup methods to remove and/or separate water, acids, bases and/or non-volatile components of these matrices are likely to be necessary for achieving reliable quantification of SVOCs in aqueous amine systems.

Derivatisation is often used to improve the sensitivity and robustness of GC analysis of thermally labile, strongly polar and alkaline analytes.[18] Many of the amines and organic degradation products present in degraded aqueous MEA absorbents are rich in hydroxyl and amino functional groups, which are traditionally difficult to quantify by GC without prior derivatisation.[18] Derivatised compounds may also be easier to identify due to the formation of larger and/or more stable characteristic fragments during mass spectrometry. The combined improvements in chromatography and mass spectrometry are likely to result in improved sensitivity and repeatability of GC-MS analyses. Silylation and acylation are common derivatisation methods for amino and hydroxyl groups while alkylation is commonly used for carboxyl groups.[18,19] However, most derivatisation reagents react with water and are unsuitable for use in these aqueous amine systems without prior separation of the analytes and the water.[18,19]

The ideal sample cleanup procedure for the analysis of organic degradation products in aqueous amine systems by derivatisation and GC-MS analysis would separate or remove: (a) the water, (b) non-volatile inorganic compounds and (c) acidic SVOCs and alkaline SVOCs. Classical extraction techniques, such as liquid-liquid extraction or SPE with hydrophobic stationary phases, are unlikely to be useful for separating the water or the polar, hydrophillic SVOCs from the aqueous MEA absorbents used for PCC of CO_2.

In this study, we compare the use of a cation exchange and a dehydration method for the cleanup of a degraded aqueous MEA absorbent for GC-MS analysis. The dehydration method employed both rotary evaporation and molecular sieves to remove the water from the degraded aqueous MEA absorbent samples. These methods were chosen to separate or fractionate the samples in different ways. The cation exchange method removed most of the water and fractionated the sample into *acids and neutrals* (neutral and negatively ionisable compounds) and the *bases* (positively ionisable compounds). The inorganic cations were likely to remain on the sulfonic acid cation exchange resin,[20] preventing them from interacting with analytes or depositing in the GC-MS injector or column. Both the *acids and neutrals fractions* and the *bases fractions* were analysed by GC-MS with and without derivatisation.

The dehydration procedure simply removed the water from each sample, with the purpose of enabling the use of derivatisation reagents that are sensitive to water. The advantage of the dehydration method was the reduced opportunity for loss of high molecular weight or strongly basic compounds. However, unlike cation exchange, the dehydration procedure did not attempt to remove heat-stable salts or non-volatile compounds from the samples and for this reason, dehydrated samples were not analysed by GC-MS without derivatisation. A more serious disadvantage of the dehydration procedure is the use of heat and vacuum to remove water which provides further opportunity for both loss of volatile analytes and further thermal degradation of aqueous amine samples.

Thus, this study aims to: (a) compare dehydration (by rotary evaporation and molecular sieves) and cation exchange, and (b) investigate the robustness of the cation exchange method for the analysis of SVOCs by GC-MS. Samples of severely degraded 30% MEA (w/w) were obtained during a six month campaign at CSIRO's PCC pilot plant at a coal-fired power station in Victoria, Australia. These samples were used to evaluate the reliability and repeatability of GC-MS quantification using these methods. For the first time, sample cleanup methods for the analysis of SVOCs in an aqueous amine system used for PCC of CO_2 from a coal-fired power station are reported.

2. MATERIALS AND METHODS

2.1 Samples

The details of the three samples obtained during a six month PCC campaign at pilot plant operated by CSIRO at AGL's Loy Yang power station are given in Table 1. These samples are the first, middle and last in a set of twelve samples obtained to investigate the middle-late stages of MEA degradation in the absence of oxidation inhibitors, corrosion inhibitors or amine reclamation. The details of the aqueous amine system, sampling procedures, pilot plant and operating conditions are given elsewhere.[21,22] To enable investigation of the effects of accumulated degradation products, a matrix blank was prepared from reagent grade MEA (>99% purity from ChemSupply, Gillman, SA, Australia) and ultra-pure water (18.2 MΩ/cm resistance, MilliQ Academic, Millipore).

Table 1. Details of the three pilot plant samples used to determine the suitability of the dehydration and cation exchange cleanup methods for GC-MS analysis.

Sample ID	**Operating hours**	**CO_2 captured (t)**	**MEA concentration (% w/w)**	**CO_2 concentration (mol CO_2/kg)**	**CO_2 lean loading (CO_2: MEA molar ratio)**	**Heat Stable Salts (% w/w, as MEA)**
A	5	0.12 ± 0.0001	35.2 ± 0.6	1.22 ± 0.01	0.212 ± 0.1	0.797 ± 0.03
B	309*	6.04 ± 0.008	30.7 ± 0.09	1.1 ± 0.004	0.219 ± 0.03	1.23 ± 0.02
C	834	14.1 ± 0.02	27.4 ± 1	0.587 ± 0.007	0.131 ± 0.2	2.29 ± 0.01

*Portions of sample B were used for comparison of dehydration and cation exchange sample treatment procedures

Initial comparisons of the dehydration and cation exchange sample cleanup methods were conducted using portions of the matrix blank and sample B. These portions were spiked with organic degradation products obtained from commercial suppliers at three different concentrations (spiking levels 1-3, Table 2). The masses of each compound added to these blank and sample matrices were chosen to cover the range of approximate concentrations measured during a previous investigation into the use of GC-MS for the analysis of SVOCs in aqueous amine systems.[23] Portions of all three samples obtained from the pilot plant and the blank matrix were also spiked at level 4 (Table 2) to assess the impact of the severity of amine degradation on the recoveries of these analytes using cation exchange, acetylation and GC-MS analysis.

2.2 Preparation of standard solutions

All standard solutions were prepared from commercially available pure compounds which were accurately weighed and dissolved in methanol (chromatography grade, from BDH, Poole, England). Up to 10% water was added to amide standards to ensure complete solvation. Standards were stored below 4°C in the dark. Internal standards were used to account for variations in sample cleanup, derivatisation and GC-MS procedures.

Analytical standards were used to calibrate the GC-MS, investigate matrix effects and determine recoveries of compounds that were: (a) available from commercial suppliers; and (b) had been previously reported in literature. The compounds used to prepare analytical standards were: diethanolamine (99%), N-acetylethanolamine (technical grade), N-(2-hydroxyethyl)-2-imidazolidione (75% in water), 1-(2-hydroxyethyl)succinimide (95%), 1-(2-hydroxyethyl)imidazole (97%), N,N'-bis-(2-hydroxyethyl)oxamide (98%), glycolic acid (>99%), glyoxylic acid (>98%) and bicine (>99%) from Sigma Aldrich, Australia; glycine (>99.5%), diethanolamine (>98.9%), formamide (>99.5%) and acetamide (>99.5%) from Chem Service (West Chester, PA, USA); and 2-oxazolidione (>97%) from Wako Pure Chemical Industries (Japan).

Prior to both cation exchange and dehydration procedures, propanoic acid, pentanoic acid and isobutylamine from Chem Service (West Chester, PA, USA) as well as malonic acid (>99.95%, Sigma Aldrich, Australia) were added to each sample or blank as surrogate standards. Propanoic acid and malonic acid were also used as internal standards for quantificaton of butyl esters. 9.5 µg of d_5-phenol (>98%) from Cambridge Isotope Laboratories (MA, USA) dissolved in chromatography grade methanol was added to each cation exchange fraction after elution and used for quantification of the methyl/acetyl derivatives. The same mass of d_5-phenol was added to subsamples of the dehydrated residue prior to derivatisation.

Table 2. Concentrations (g/kg) of analytes added to blank and sample matrices

Compound name	**CAS number**	**Abb.**	**Spiking levels**			
			1	**2**	**3**	**4**
Organic acids						
Acetic acid	64-19-7		9.92	0.989	0.099	4.970
Formic acid	64-18-6		10.3	1.031	0.104	5.180
Oxalic acid	144-62-7		0	0	0	0.106
Glycolic acid	79-14-1		2.34	0.233	0.023	0.115
Semi-volatile organic compounds						
Formamide	75-12-7		2.38	0.238	0.0238	1.190
Acetamide	60-35-5		1.71	0.171	0.0171	0.856
Bicine	150-25-4		1.83	0.183	0.0183	0.914
N-acetylethanolamine	142-26-7	HEA	2.09	0.209	0	1.050
N,N’-bis(2-hydroxyethyl)oxamide	1871-89-2	BHEOX	1.66	0.166	0	0.828
N-(2-hydroxyethyl)succinimide	18190-44-8	HES	2.08	0.208	0.0208	1.040
2-(2-hydroxyethylamino)ethanol	111-41-1	HEEDA	3.10	0.310	0.0310	1.550
1-(2-hydroxyethyl)imidazole	1615-14-4	HEI	2.20	0.220	0.0220	1.100
N-(2-hydroxyethyl)-2-imidazolidione	3699-54-5	HEIA	2.76	0.276	0.0276	1.380
Oxazolidione	497-25-6	OZD	2.18	0.218	0.0218	1.090
Diethanolamine	111-42-2	DEA	11.0	1.10	0.110	5.490

2.3 Sample cleanup methods

The two sample cleanup methods summarized in Figure 1 were compared using portions of sample B (Table 1) and the matrix blank. Triplicate portions of sample B and the matrix blank were prepared for GC-MS analysis by both cation exchange and dehydration procedures without the addition of spiking standards. Single portions of sample B and the matrix blank were also spiked (Table 2, levels 1-3) prior to cation exchange and dehydration procedures.

To investigate the robustness of the cation exchange method, duplicate portions of the three samples (A, B and C) and the matrix blank were analysed. Single portions of the three samples and the matrix blank were also spiked at level 4 (Table 2) prior to cation exchange.

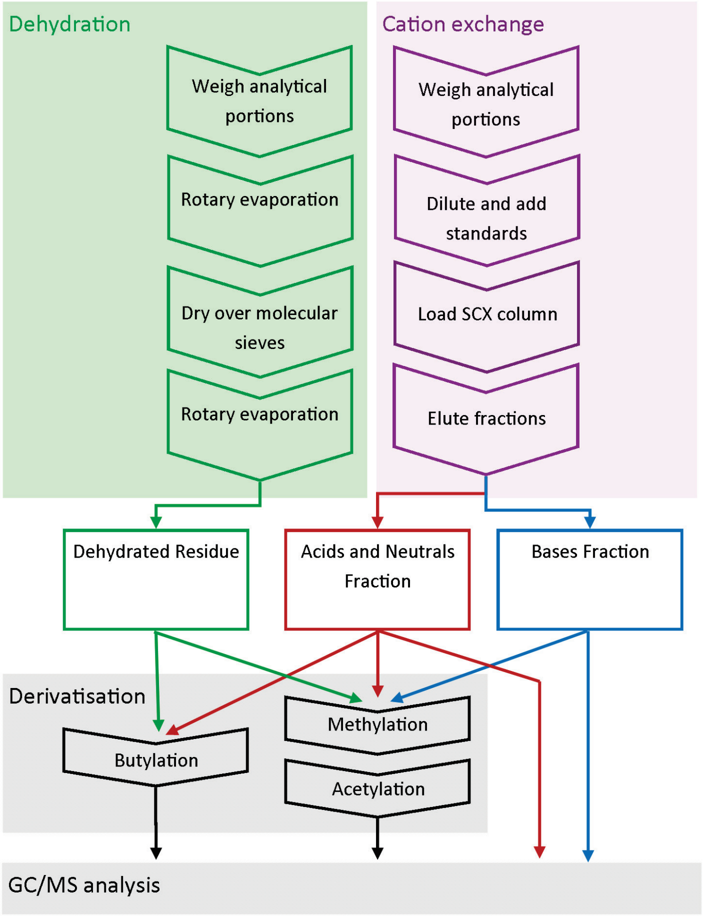


Figure 1. Flowchart of sample cleanup and derivatisation procedures used for the quantification of organic degradation products in the 30% (w/w) MEA aqueous amine system by GC-MS

2.3.1 Cation exchange

Anhydrous Na_2SO_4 (approximately 100 mg, >99% from Merck, Kilsyth, Victoria, Australia; calcined at 400°C overnight prior to use) was added to the top of each strong cation exchange (SCX) SPE cartridge (DSC-SCX, 500 mg, 3 mL from Sigma Aldrich, Australia) prior to conditioning with 6 mL of methanol. After elution of the first 3 mL of methanol, the flow was stopped for at least 5 min. All liquid flow-rates through the SPE cartridges were approximately 0.5 mL/min. Approximately 50 mg of each sample was accurately weighed into a clean vial, diluted with 500 µL of methanol, fortified with appropriate standards and loaded onto the conditioned SPE cartridge. Collection of the *acids and neutrals fraction* commenced immediately before loading the sample onto the cartridge and continued until a further 1 mL of methanol (equivalent of two bed volumes) was completely eluted. The SPE cartridges were dried under vacuum for 30 min before the *bases fraction* was eluted with 3 mL (equivalent of six bed volumes) of 5% ammonium hydroxide (prepared from 35% ammonium hydroxide in water from BDH, Poole, England) in methanol. After addition of internal standard (d_5-phenol), fractions were stored in amber, silanised vials at 4°C.

2.3.2 Dehydration

Approximately 5 g of sample was accurately weighed into a clean 25 mL round bottom flask. Each sample was rotary evaporated at 60°C, 150 mbar with a nitrogen purge for 5 min. The residue was dissolved in methanol and dried over 2 g of 3A molecular sieves (1/16" pellets from BDH, Poole England, extracted with methanol and heated at 260°C overnight prior to use) in the dark overnight. After separating the molecular sieves from the methanol solution, the molecular sieves were rinsed three times with approximately 2 mL methanol. The methanol solutions were combined, filtered through 0.2 µm hydrophilic PTFE syringe filters (Membrane Solutions, Dallas, TX, USA) and rotary evaporated at 60°C, 330 mbar with a nitrogen purge. The residues were weighed, transferred to amber silanised vials and stored below 4°C.

2.4 Derivatisation

Two derivatisation procedures (Figure 1) were used for volatile organic acids (butyl esterification) and other organic degradation products (sequential methylation and acetylation). The details of the procedures are given in the following sections.

2.4.1 Butyl esterification

Organic acids in *acids and neutrals fractions* and dehydrated samples were derivatised with 15% BF_3 in n-butanol (Sigma Aldrich, Australia) prior to analysis by GC-MS using propanoic acid and malonic acids as internal standards. Approximately 200 µL of each *acids and neutrals fraction* was evaporated under a gentle stream of nitrogen to remove the methanol. 200 µL of 15% BF_3 in n-butanol was added and the mixture was heated in a sealed vial at 80°C for 60 min. After cooling and adding 200 µL of n-hexane, the reaction mixture was rinsed three times with 0.5 mL ultra-pure water. A larger scale reaction was used for the dehydrated sample residues because it was difficult to obtain subsamples smaller than 10 mg. Between 10 and 30 mg of the dehydrated residue was accurately weighed into a 5 mL reaction vial and mixed with 1 mL of 15% BF_3 in n-butanol. After heating at 80°C for 60 min, cooling and adding 1 mL of n-hexane, the reaction mixture was rinsed three times with 1 mL of ultra-pure water.

2.4.2 Methylation and acetylation

Subsamples of the dehydrated residues and *acids and neutrals fractions* (Figure 1) were sequentially derivatised with diazomethane and either trifluoroacetic anhydride or acetic anhydride. Diazomethane was generated in a Wheaton Micromolar apparatus using diethyl ether, 1-methyl-3-nitro-1-nitrosoguanidine (Wako Pure Chemical Industries, Japan), sodium hydroxide (Rowe Scientific) and ultra-pure water. 200 µL aliquots of diazomethane in diethylether were added to subsamples of dehydrated residues and cation exchange fractions and complete methylation of pentanoic acid and malonic acids was confirmed by GC-MS. Residual methanol and diethylether were evaporated under nitrogen prior to acetylation.

Trifluoroacetic anhydride (>99%) and acetic anhydride (>99%) were obtained from Sigma Aldrich (Australia). 200 µL of dichloromethane (chromatography grade) was added to each residue prior to the addition of 200 µL of trifluoroacetic anhydride. The reaction was allowed to proceed at room temperature overnight prior to evaporation under nitrogen, dilution of the residue in dichloromethane and analysis by GC-MS. Non-fluorinated acetyl derivatives were prepared by dissolving each residue in 200 µL of pyridine prior to the addition of 200 µL of acetic anhydride. The reaction was heated to 80°C overnight. Prior to GC-MS analysis, the reaction mixtures were evaporated under nitrogen and redissolved in dichloromethane. The completeness of each reaction was confirmed by the complete acetylation of the d_5-phenol internal standard.

2.5 GC-MS analyses

The butyl esters were analysed using a Varian 3800 GC and Varian Saturn 2200 ion-trap MS. The samples were injected using an 8400 autosampler into a 1177 injector with a deactivated focus liner from SGE (Australia). The GC column was a CP-Sil 8 CB for Amines 30 m × 0.32 mm × 1.0 µm from Agilent (Netherlands). The injector split was 1:10 and the helium carrier gas flow was 1.5 mL/min. The injector temperature was 280°C and the column oven temperature program started at 50°C for 2 min, increased to 60°C at 2°C/min followed by a 20°C/min increase to 320°C and held at 320°C for 4 min. The mass spectrometer scanned from 29 *m/z* to 200 *m/z* between 5 min and 10 min and scanned from 29 m/z to 400 m/z from 10 min to 28 min.

The same GC-MS system was used for analysis of the acetyl derivatives with the following parameters. The injector split was closed for the first 0.7 min, immediately opened to 1:100, and reduced to 1:10 after 2 min. The helium carrier gas pressure was 5 psi during injection and for the first 0.8 min. During the remaining analysis time, the helium carrier gas flowrate was 1.5 mL/min. The injector temperature was 280°C and the column oven temperature program started at 80°C for 1 min, then increased to 150°C at 10°C/min, increased to 320°C at 15°C/min and remained at 320°C for 5 min. The mass spectrometer scanned from 35 *m/z* to 300 *m/z* from 3 min to 9 min, and 40 *m/z* to 450 *m/z* from 9 min to 25 min. The ion source was turned off during elution of the MEA acetyl derivative.

Prior to the analysis of each batch of samples, analytical standards were analysed to ensure the resolution, peak shapes and intensities of analytical standards were acceptable. Analytical standards were also analysed regularly during each batch of samples and the internal and surrogate standards were used to monitor any going deterioration in peak shapes, intensities and resolution of the GC-MS chromatograms.

2.6 Ion chromatography

Organic acids were quantified as described in chapter 5.[11]

2.7 Recovery, repeatability and precision calculations

After sample preparation and derivatisation, each sample portion was analysed by GC-MS in triplicate. These triplicate analyses were averaged prior to calculation of the pooled average concentrations, relative percent deviations, and recoveries. Relative percent differences (%RPD) were calculated as the mean deviation divided by the average and expressed as a percentage.

Two types of recoveries (matrix-free and matrix-matched) were calculated for the compounds listed in Table 2 and are expressed as percentages. Matrix-free recoveries were calculated as the ratio of the concentration measured in each matrix and the measured concentration of a standard in the analytical solvent (methanol for underivatised compounds, n-hexane for butyl derivatives and dichloromethane for methyl, acetyl derivatives). The matrix-matched recoveries were calculated as the ratio of the concentrations measured in the spiked samples and the concentration measured in the spiked matrix blank [i.e. 30% (w/w) aqueous MEA]. Where appropriate, the measured concentrations were corrected for the concentration of the analyte in the unspiked blank and sample matrices.

Each recovery calculation provided information about the effects of specific components of the matrices. The matrix-free recoveries from the blank matrix measured the effects of water and MEA on the concentrations of analytes measured by GC-MS. Matrix-free recoveries from the sample matrix incorporated the effects of all the matrix components including water and MEA. The matrix-matched recoveries measured the effects of all matrix components other than water and MEA.

The concentrations measured in replicate portions of sample B were used to compare the repeatability of GC-MS analyses following the dehydration and cation exchange procedures. The use of concentrations measured in replicate portions of real samples without the addition of target analytes ensured that the %RPD measurements: (a) incorporated variations in matrix components; and (b) were measured at concentrations that are typical of samples from degraded aqueous amine systems.

Organic acids (formate, acetate and oxalate) were included in this study because well-established analytical methods, other than GC-MS, are available for the quantification of these compounds in aqueous amine systems. Ion chromatography is routinely used for the analysis of small organic acids in aqueous matrices and modern instruments are well able to separate and quantify the small organic acids that are likely to be present in degraded aqueous amine systems.[7] This enables validation of the cation exchange and dehydration procedures using an independent analytical method. For this reason, the concentrations of acetic and formic acids measured by ion chromatography are used to validate the concentrations measured as butyl esters by GC-MS following cation exchange and dehydration.

3. RESULTS AND DISCUSSION

The benefits of three sample preparation methodologies were considered: (a) cation exchange cleanup only; (b) dehydration with derivatisation; and (c) cation exchange with derivatisation. Both dehydration and cation exchange sample cleanup methods removed water and CO_2 species from the MEA absorbent samples. The dehydration method used vacuum and heat to desorb CO_2 while the cation exchange method used Na_2SO_4 to absorb water and small bubbles of CO_2 were observed rising from the top of the cation exchange resin during SPE. The removal of water enabled the use of water-sensitive derivatisation reagents and the removal of CO_2 during sample preparation eliminated any opportunities for CO_2 species to interfere with quantification of organic analytes by GC-MS.

Table 3 shows the improvements in sensitivity and linear concentration range achieved by using derivatisation prior to GC-MS analysis of standard solutions. The repeatability and analyte recoveries used to compare the various cleanup and derivatisation procedures for the GC-MS analysis of organic degradation products in these degraded 30% (w/w) aqueous MEA absorbents are shown Tables 4 and 5. Table 4 compares the use of ion chromatography (a well-established, independent technique) with the novel dehydration and cation exchange sample cleanup techniques with GC-MS for the quantification of organic acids.

The initial comparison of dehydration and cation exchange sample cleanup methods is presented in Table 5. This comparison was conducted using portions of a blank matrix [30% (w/w) MEA] and sample B (Table 1). Following this initial comparison, the cation exchange sample cleanup method was chosen for further investigation of the effects of degradation severity on the repeatability and accuracy of GC-MS analysis using samples A, B and C (Table 1).

3.1 Derivatisation of analytes

Many of the target compounds in Table 3 are highly polar and alkaline. They are also difficult to analyse by GC-MS and could not be calibrated without derivatisation (Table 3). Derivatisation enabled the analysis of all these compounds by GC-MS. The linear regression coefficients of calibration curves for each of these compounds (where possible) and their derivatives are listed in Table 3.

Initially, trifluoroacetic anhydride was the preferred reagent because it is more volatile and more reactive than acetic anhydride. The use of trifluoroacetic anhydride significantly improved the peak shapes of many SVOCs but, during the analysis of trifluoroacetyl derivatives of the cation exchange fractions, the MS spectral data quality rapidly degraded and recoveries are only reported in Table 3 where MS data of sufficient quality was available. When non-fluorinated acetic anhydride was used to acetylate the dehydrated sample residues, the

MS spectral quality did not degrade during the analysis. This suggests that the fluorinated derivatives were reactive or induced space charge effects during the storage and ejection cycles of the ion-trap mass spectrometer used in this study. For this reason, non-fluorinated acetic anhydride was used to derivatise all acetylated standards and samples unless specified otherwise.

To increase the molecular mass and volatility of organic acids, formate, acetate and oxalate were converted to butyl esters prior to GC-MS analysis. The butyl ester of formic acid was not well separated from residual butanol using this GC-MS system, resulting in a slightly lower regression coefficient (Table 3) compared to the other butyl esters. The butyl ester of glycolic acid was also detected in standard solutions but the peak shape rapidly deteriorated and could not be calibrated.

2-oxazolidione (OZD), N-acetylethanolamine (HEA), formamide and acetamide are the only SVOCs in Table 3 that were not analysed as the acetyl derivatives. HEA was not calibrated after derivatisation because the acetyl derivative of HEA is identical to the acetyl derivative of MEA. Formamide and acetamide were not quantified after derivatisation because they were likely to be lost when the acetylation reagents were removed by evaporation. However, OZD was not calibrated as the acetyl derivative because the efficiency of the acetylation was found to be dependent on the concentration of OZD and the presence of MEA. In the absence of MEA, the underivatised OZD was successfully calibrated (Table 3) and the derivatisation efficiency of OZD was consistent in the calibration standards and *acids and neutrals fractions*. However, in the presence of MEA the derivatisation efficiency of OZD increased to almost 100%. For this reason, the concentrations of OZD were not measured in the *bases fractions* or dehydrated residues (Table 5).

Bicine is the only SVOC in Table 3 with a carboxylic acid functional group in addition to hydroxyl and amino functional groups. Methanol was used as a solvent during both sample cleanup procedures and residual methanol resulted in partial methylation (by acid catalysed transesterification) of carboxylic acids during initial acetylation trials. To ensure complete methylation, all samples and standards were methylated prior to acetylation.

Both the mono- and bisacetyl derivatives of N-(2-hydroxyethyl)imidazolidione (HEIA) were formed under the deriviatisation and GC-MS conditions used in this study. Table 3 shows that both HEIA derivatives were successfully calibrated, indicating that the ratios of mono- and bisderivatives were consistent and repeatable in pure standards. However, the ratios of the mono- and bisacetyl derivatives produced by derivatisation and GC-MS analysis of samples containing HEIA varied. Both derivatives remained quantifiable by GC-MS and the concentration of HEIA in each sample was calculated from the sum of the mono- and bisacetyl derivatives.

Two of the SVOCs in Table 3 (2-(2-hydroxyethylamino)ethanol, HEEDA; and diethanolamine, DEA), could not be calibrated in analytical solvents (isopropanol or methanol) without derivatisation. HEEDA could not be detected below 1000 mg/L in either solvent. However, Table 3 shows that the acetyl derivatives of these compounds all produced linear calibration curves with regression coefficients of >0.97.This clearly demonstrates the potential benefits of derivatisation for the GC-MS analysis of organic degradation products in aqueous amine systems.

Table 3. Summary of the calibration parameters and cation exchange fractionation of previously identified organic degradation products from the 30% (w/w) MEA aqueous amine system

Compound name	Abbreviation	CAS number	Calibration range			Calibration co-efficient			Cation exchange fraction	
			Underivatised (mg/L)	Butyl esters	Methyl,acetyl derivatives (mg/L)	Underivatised	Butyl esters	Methyl,acetyl derivatives	Acids	Bases
Malonic acid§		141-82-2	---	---	1-100	---	---	0.949	●	
Isobutylamine§		78-81-9	---	---	10-75	---	---	0.890		●
Acetate		64-19-7	---	4-250	---	---	0.995	---	●	
Formate		64-18-6	---	5-520	---	---	0.969	---	●	
Formamide		75-12-7	1.2-240	---	---	0.999	---	---	●	
Acetamide		60-35-5	8.6-170	---	---	0.991	---	---	●	
Bicine		150-25-4	9.2-1800	---	18-3700	0.979	---	0.992		●
N-acetylethanolamine	HEA	142-26-7	21-2100	---	---	0.998	---	---	○	○
N,N-bis(2-hydroxyethyl)oxamide	BHEOX	1871-89-2	8.3-1700	---	17-3300	0.952	---	0.984	●	
N-(2-hydroxyethyl)succinimide	HES	18190-44-8	11-2100	---	21-2100	0.995	---	0.997	○	○
2-(2-hydroxyethylamino)ethanol	HEEDA	111-41-1	---	---	31-3100	---	---	0.976		●
1-(2-hydroxyethyl)imidazole	HEI	1615-14-4	110-2200	---	11-11000	0.979	---	0.985		●
N-(2-hydroxyethyl)-2-imidazolidione	HEIA	3699-54-5	140-2800	---	28-1400$^{\#}$ 28-5500$^{\#\#}$	0.996	---	0.997$^{\#}$ 0.993$^{\#\#}$	○	○
Oxazolidione	OZD	497-25-6	11-2200	---	22-11000^	0.997	---	0.976^	●	
Diethanolamine	DEA	111-42-2	---	---	110-550	---	---	0.976		●

● 100% recovered from this fraction; ○ Variable fractionation; --- not measured; ^ underivatised compound; $^{\#}$monoacetyl derivative; $^{\#\#}$bisacetyl derivative; §surrogate standard.

Table 4. Comparison and validation of dehydration and cation exchange procedures for the analysis of formic and acetic acids by butylation and GC-MS

	Formic acid		**Acetic acid**	
	Concentration (g/kg)*	**%RPD**	**Concentration (g/kg)***	**%RPD**
Blank matrix				
Ion chromatography	0.603	7	0.978	1
Cation exchange	2.0 (0.61)	20	1.2	22
Dehydration	0.34 (0.10)	15	0.047	16
Sample B				
Ion chromatography	4.662	<1	3.13	<1
Cation exchange	14 (4.1)	25	3.1	27
Dehydration	7.1 (2.1)	<1	0.66	7

*The values within brackets are multiplied by 0.3 to correct for 300% matrix-free recovery

Table 5. Comparison of dehydration and cation exchange for the analysis of organic degradation products by derivatisation and GC-MS

Compound name	Abbreviation	CAS number	Cation exchange									Dehydration		
			Underivatised			Butyl or trifluoroacetyl derivatives			Butyl or acetyl derivatives			Butyl or acetyl derivatives		
			Blank matrix	Matrix-matched	%RPD^	Blank matrix	Matrix-matched	%RPD^	Blank matrix	Matrix-matched	%RPD^	Blank matrix	Matrix-matched	%RPD^
Malonic acid§		141-82-2	---	---	---	---	---	---	B	A	7	---	---	---
Isobutylamine$^{§\#}$		78-81-9	---	---	---	---	---	---	C	A	12	---	---	---
Acetate		64-19-7	---	---	---	A	B	25	B	A/D/E	83	B	B	7
Formate		64-18-6	---	---	---	D	A	27	B	A/E	56	D	B	<1
Formamide		75-12-7	D	B	4	---	---	---	---	---	---	---	---	---
Acetamide		60-35-5	B	A	ND	---	---	---	---	---	---	---	---	---
Bicine		150-25-4	D*	D*	14	A	A	---	A	A/D	ND	D	C	---
N-acetylethanolamine	HEA	142-26-7	C/E	D*	8	---	---	---	---	---	---	---	---	---
N,N-bis(2-hydroxyethyl)oxamide	BHEOX	1871-89-2	---	---	---	---	---	---	D	E	12	D	E	ND
N-(2-hydroxyethyl)succinimide	HES	18190-44-8	E	A*	11	B	A	---	A	A/D	9	C/D	B/D	22
2-(2-hydroxyethylamino)ethanol	HEEDA	111-41-1	---	---	---	A	A	---	A	D	ND	D*	A*	ND
1-(2-hydroxyethyl)imidazole	HEI	1615-14-4	A	D	<1	---	---	---	E	D	5	D	D/E	14
N-(2-hydroxyethyl)-2-imidazolidione	HEIA	3699-54-5	---	---	---	---	---	---	A	C	6	D	B/E	3
2-oxazolidione	OZD	497-25-6	B	A/D	2	---	---	---	A	A	<1	---	---	---
Diethanolamine	DEA	111-42-2	---	---	---	---	---	---	A	D	ND	C/E	B/E	ND

A, 80-120% at both1 and 2 spike levels; B, 70-130% at both 1 and 2 spike levels; C, 50-150%; D, >150%; E, <50%; ^measured from duplicate portions of sample B; §surrogate standards; *Not recovered at spike level 2; --- not measured; ND, not detected.

Table 6. The effects of the severity of aqueous amine system degradation on the recovery and repeatability of organic degradation products measured by cation exchange, acetylation and GC-MS

	Malonic acid	Isobutyl amine	Formic acid	Acetic acid	Oxalic acid	Bicine	BHEOX	HES	HEEDA	HEI	HEIA	OZD	DEA
Concentration (g/kg)													
Matrix blank	NR	NR	ND	ND	ND	ND	ND	ND	ND	0.07	0.055	ND	ND
Sample A	NR	NR	3.9	0.90	1.7	ND	0.27	0.22	ND	0.40	0.11	ND	ND
Sample B	NR	NR	6.1*	0.51*	3.6*	ND	0.29	0.04*	ND	0.54	0.18	0.09	ND
Sample C	NR	NR	7.8*	0.12*	7.5*	ND	0.46	0.24	ND	2.4	0.28	0.09	ND
Repeatability (%RPD)													
Matrix blank	10	5	NA	NA	NA	NA	NA	NA	NA	<1	33		NA
Sample A	<1	18	17	22	17	NA	58	83	NA	4	35		NA
Sample B	7	12	56	83	16	NA	12	3	NA	5	6	<1	NA
Sample C	13	4	34	82	100	NA	19	48	NA	8	4	4	NA
Matrix-free recovery (%) at spike level 4 (ca. 1.0 g/kg)													
Matrix blank	72	21	71	70	NR	101	181	111	122	25	100	90	105
Sample A	74	16	9	31	154	94	46	121	103	73	105	95	115
Sample B	69	17	74	82	171	296	47	226	116	222	124	96	323
Sample C	67	14	118	143	388	163	50	130	111	523	138	98	531
Matrix-matched recovery (%)at spike level 4 (ca. 1.0 g/kg)													
Sample A	102	78	12	43	NA	90	25	106	82	284	102	103	107
Sample B	95	81	104	118	NA	295	26	206	96	894	125	108	312
Sample C	93	66	94	201	NA	163	28	118	91	2103	139	110	511

NA, not applicable; ND, not detected; NR, not reported; * measured as butyl esters.

3.2 Comparison of dehydration and cation exchange sample cleanup methods

In the following sections, the suitability of dehydration and cation exchange sample cleanup methods for the analysis of the organic acids and SVOCs in aqueous amine systems are evaluated. Firstly, the recoveries, repeatability and bias of the organic acid concentrations measured by butylation with GC-MS analysis are considered separately and compared with the concentrations measured by ion chromatography. Secondly, the recovery and repeatability of SVOCs following cation exchange and GC-MS analysis without derivatisation are assessed. The third section uses recoveries and repeatabilities of all the target analytes in Table 2 measured by GC-MS with derivatisation to: (a) compare dehydration and cation exchange sample cleanup techniques; and (b) investigate the effects of the severity of the aqueous amine system degradation on the analysis of SVOCs by cation exchange, derivatisation and GC-MS. Most compounds were not recovered after spiking the matrix blank at level 3 (Table 2) and for the sake of clarity, these results are not discussed or reported in Tables 5 or 6. However, recoveries for spiking level 3 are available in the supplementary information.

3.2.1 Comparison and validation of dehydration and cation exchange sample preparation methods for the analysis of organic acids by GC-MS

Both formate and acetate were recovered following both cation exchange and dehydration sample cleanup procedures. The matrix-free and matrix-matched recoveries (Table 5) of acetate were within 70-130% for both cation exchange and dehydration sample cleanup methods. The acceptable matrix-matched recoveries indicate that the components (other than water and MEA) in the degraded sample B did not have a significant impact on the recovery of acetate. Interestingly, widely variable (<50% to >150%) matrix-matched recoveries were measured using cation exchange, butylation and GC-MS analysis, indicating that the matrix components of other samples may significantly impact on the recovery of acetate from degraded aqueous amine systems.

The matrix-free and matrix-matched recoveries of acetate from sample B are consistent with the excellent agreement between the concentration of acetate measured by cation exchange, butylation and GC-MS analysis and ion chromatography, as shown in Table 4. The concentrations of acetic acid measured following cation exchange deviated by less than 4% from the concentration measured by ion chromatography for both the blank and sample B matrices. The higher %RPD of the acetic acid concentrations measured following cation exchange reflect the greater complexity of the cation exchange procedure compared to ion chromatography.

Contrastingly, Table 4 shows the acetate concentrations measured by ion chromatography were higher in both the blank and sample B compared to the acetate concentrations measured by dehydration, butylation and GC-MS. This is consistent with the <100% matrix-matched recoveries of acetate (Supplementary information, 75% and 79% at 1 g/kg and 10 g/kg respectively). The low recoveries of acetate from the dehydration sample cleanup procedure are most likely due the co-distillation of acetate with the water removed during the sample cleanup step.

The matrix-free recoveries of formate following cation exchange and dehydration were higher than 150% (Table 5) and consistently close to 300% (excluding one outlier, the average of the remaining seven matrix-free recoveries was 290% with a %RPD of 12%). However, on a matrix-matched basis, the formate recoveries using both techniques were within 70-130% for sample B. Together, these recoveries indicate that the measured formate concentrations overestimated the true concentrations by 300%. High recoveries were measured using both dehydration and cation exchange procedures, indicating that the derivatisation procedure (e.g. presence of formylbutanoate as a reaction artifact or an impurity in the BF_3:n-butanol) or GC-MS conditions (e.g. co-elution of a reaction product, artifact or impurity with formylbutanoate) are the most likely causes. A small co-eluting peak was present in the procedural blanks used to monitor the butylation procedure, but it was not sufficient to cause a 300% increase in the measured formic acid concentration. This suggests a derivatisation artifact or reagent impurity is unlikely to be the cause of the high formate recoveries. The most probable explanations include continued the production of formate (e.g. during cleanup and analysis of the MEA absorbent) or co-elution of another organic acid or derivatisation reaction product.

Table 4 shows the corrected formate concentrations measured following cation exchange deviated by less than 12% from the concentrations measured by ion chromatography, demonstrating excellent agreement. The concentrations of formate measured by GC-MS following dehydration and butylation were significantly lower than the concentrations of formate measured by ion chromatography after correcting for 300% recoveries. The erroneously low measured concentrations of formate are likely to be due to evaporation of formate during the use of heat and vacuum to remove water from the sample.

The repeatability of both formate and acetate concentrations measured following dehydration were slightly better than the repeatability of the same measurements following cation exchange (Table 4). This is likely to be as a result of the larger scale of the reaction and the larger masses of organic acids present in the hexane extracts following dehydration. This indicates that the repeatability measurements of both formate and acetate concentrations following cation exchange could be improved by derivatising more than one-tenth of the *acids and neutrals fraction* prior to GC-MS analysis. However, neither cation exchange nor dehydration procedures were as repeatable or reliable as ion chromatography for the quantification of formic acid in degraded 30% MEA solvents.

Overall, the cation exchange procedure demonstrated excellent agreement with the ion chromatography for the measurement of formate and acetate in the degraded aqueous amine system. This is an important indication that the cation exchange sample preparation procedure may be suitable for the analysis of other organic compounds in aqueous amine systems by GC-MS. The dehydration procedure is not a suitable sample preparation procedure for the analysis of formate and acetate because of the co-distillation of these volatile organic acids under the conditions required to remove the water from the aqueous amine system.

3.2.2 Recoveries of SVOCs using cation exchange and GC-MS analysis without derivatisation

SVOCs were not measured in the dehydrated residues without derivatisation and for this reason, recoveries without derivatisation are only reported for the cation exchange sample preparation procedure in Table 5. The recoveries of underivatised DEA, bicine and BHEOX could not be measured because the peak shapes deteriorated rapidly and the calibration curves of these compounds were not stable during sample analyses. The peak shapes of other underivatised basic analytes (e.g. N-(2-hydroxyethyl)succinimide, HES and 1-(2-hydroxyethyl)imidazolidinone, HEIA) also deteriorated during batches of analyses but are reported in Table 5 because their calibration curves were linear (R^2>0.99, Table 3) over several orders of magnitude and the calibration curves remained stable during analysis of samples. The analyte with the most stable peak shape during analysis of standards and samples was OZD.

The only analytes detected by GC-MS in the *acids and neutrals fractions* without derivatisation were formamide, acetamide and OZD. Acetamide was also present in the *bases fractions* but formamide could not be measured in these fractions because it co-eluted with MEA. Matrix-matched recoveries for formamide and acetamide ranged from 80% to 120% (Table 5), indicating that matrix components other than water and MEA in sample B did not significantly impact the GC-MS measurements. However, the low matrix-free recoveries of both compounds (<50%, Table 5) indicate that the cation exchange and GC-MS procedures could not accurately measure formamide or acetamide in this aqueous amine system without the use of a recovery correction factor. The low matrix-free recoveries of these volatile amides may be a result of the evaporation during drying of the cation exchange resin prior to elution of the *bases fraction*.

Very low matrix-free recoveries were also measured for HEA and HES (<50%, Table 5) in the *bases fractions.* However, HES was measured in both cation exchange fractions following derivatisation. This indicates that the reason for the low matrix-free recovery of HES was the inability of the GC-MS to measure this compound in the *acids fractions* without derivatisation. Even so, Table 5 shows that the matrix-matched recovery for HES was within 80-120% at 2 g/kg and the %RPD of triplicate measurements of sample B were less 20%, indicating that: (a) the distribution of HES between the two cation exchange fractions was consistent; and (b) neither the measured concentration nor the cation exchange fractionation were influenced by the matrix components of sample B. The variable recoveries of HEA in Table 5 may a result of additional HEA production by condensation of MEA and acetate (which was also added to spiked samples). However, HEA is a heat-stable salt and is commonly measured as acetate following alkaline hydrolysis.[11]

Accurate measurement of the HEI concentration in the matrix blank was demonstrated in Table 5 by matrix-free recoveries from the blank matrix of between 100% and 120%. However, the high matrix-matched recoveries (>150%) and the excellent repeatability (RPD <1%) of the HEI concentration measured in three portions of the sample B indicates that HEI may be subject to a strong, repeatable matrix-induced enhancement effect despite the separation of acids from bases and the removal of inorganic cations.

Table 5 also shows that OZD was also accurately measured in the blank matrix (70-130%) despite a high recovery (>150%) of OZD spiked into the sample B. For this reason, GC-MS is not suitable for the analysis of OZD after cation exchange without derivatisation unless a suitable matrix-induced enhancement effect correction factor is used.

The only analyte listed in Table 5 that could be quantified using cation exchange and GC-MS without derivatisation was acetamide. OZD and HEI could possibly be quantified with the use of a suitable matrix-induced enhancement effect correction factor. The use of cation exchange to separate positively and negatively ionisable compounds in addition to removing positively ionisable inorganic compounds was insufficient to enable the reliable quantification of many SVOCs in this degraded aqueous amine system. To improve the volatility of thermally labile compounds and reduce interactions between the analytes and the GC-MS system, derivatisation procedures were adapted.

3.2.3 Comparison of dehydration and cation exchange sample preparation procedures for the analysis of SVOCs by derivatisation and GC-MS

The superior separation of matrix components combined with the excellent agreement between the concentrations of formate and acetate measured by ion chromatography and cation exchange, butylation with GC-MS analysis indicate that cation exchange is the preferred sample preparation technique for the analysis of most analytes by use of GC-MS. For these reasons, Table 6 summarises effects of degradation severity on the repeatability and recoveries of organic degradation products in aqueous amine systems measured by cation exchange, acetylation and GC-MS. The recoveries and repeatability of analytes in sample B measured during this investigation are also included in Table 5 to provide a more complete comparison of the cation exchange and dehydration sample cleanup methods despite difficulties in measuring the analyte concentrations in the cation exchange fractions following trifluoroacetylation. The advantages and disadvantages of dehydration and cation exchange sample preparation techniques for each target SVOC analytes are discussed in the following sections.

The target SVOCs identified in the GC-MS chromatograms in Figure 2 are present alongside a large number of other organic degradation products. The identification of compounds other than the target SVOCs listed in Tables 2-6 are beyond the scope of this study. The chromatograms in Figure 2 illustrate the excellent separation of SVOCs in degraded aqueous amine systems achieved by cation exchange. The use of a smaller diameter (e.g. 0.25 mmID) column would be suitable for the analysis of these derivatised SVOCs dissolved in dichloromethane and would improve the GC-MS resolution of both the target SVOCs and other unidentified organic degradation products by decreasing the mass transfer coefficient between the gas and liquid phases.

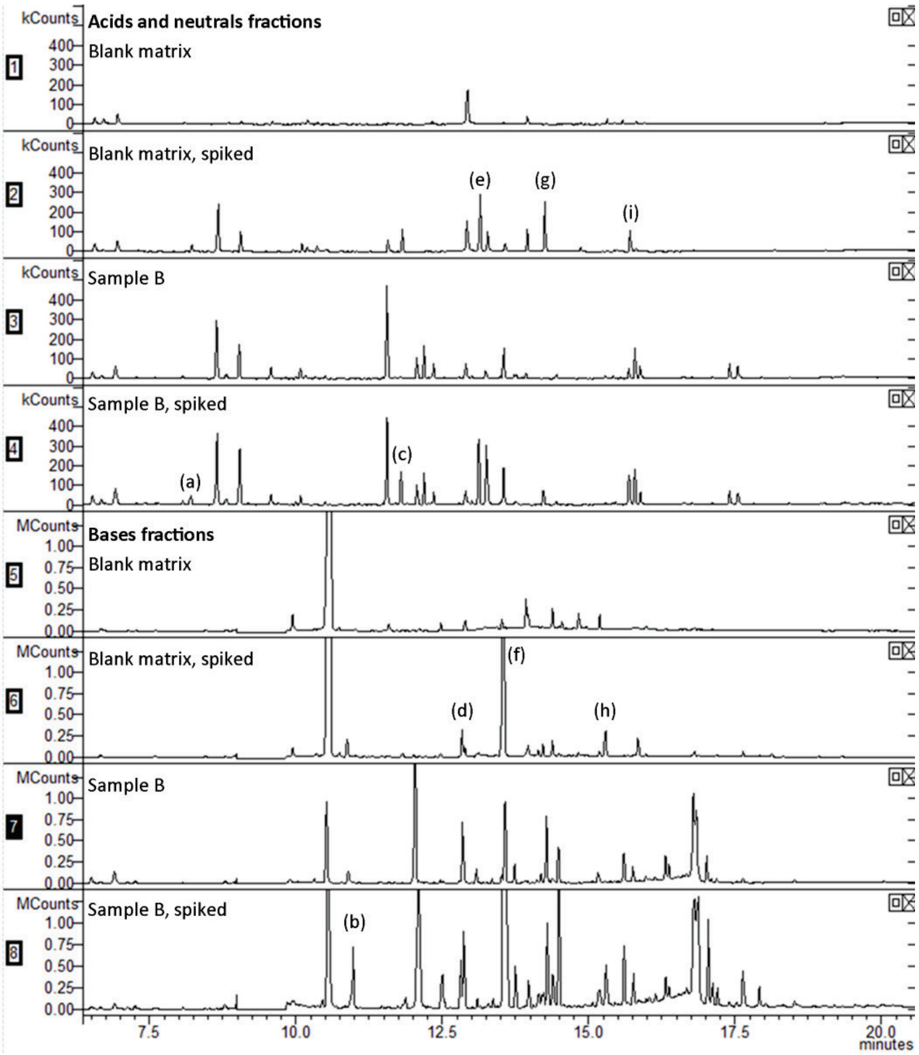


Figure 2. Comparison of GC-MS chromatograms of blank and sample B separated by cation exchange and derivatised with acetic anhydride. For the sake of clarity, the scale of the MS response on the vertical axis is smaller for the *acids and neutrals fractions* than the *bases fractions*. (a) 2-oxazolidione, OZD; (b) N-(2-hydroxyethyl)imidazole, HEI; (c) N-(2-hydroxyethyl)succinimide, HES; (d) bicine; (e) N-(2-hydroxyethyl)imidazolidione, HEIA (mono-acetyl derivative); (f) diethanolamine, DEA; (g) N-(2-hydroxyethyl)imidazolidione , HEIA(bis-acetyl derivative); (h) 2-(2-hydroxyethylamino)ethanol, HEEDA; (i) N,N'-bis(2-hydroxyethyl)oxamide, BHEOX.

3.2.3.1 Surrogate standards

Further evidence for the effectiveness of the cation exchange and acetylation procedures is provided by the recoveries of surrogate standards (isobutylamine and malonic acid) in Tables 5 and 6. The derivatives of these surrogate standards were measured in the appropriate cation exchange fractions after acetylation (malonic acid dimethyl ester in the *acids and neutrals fraction* and N-acetyl-isobutylamine in the *bases fraction*) but were not recovered from dehydrated samples. The matrix-free (69-74%) recoveries for malonic acid dimethyl ester in Table 6 were consistent but low. However, the excellent matrix-matched recoveries (93-102%) and the consistency of the matrix-free recoveries indicate that accurate quantification could be achieved by using a correction factor or matrix-matched standards. The matrix-free recoveries of isobutylamine were also low (14-

21%) and matrix-matched recoveries ranged from 66% to 81%. Considering the low correlation coefficient (Table 4) and the opportunities for isobutylamine to bond strongly to the cation exchange resin and/or glass surfaces, these recoveries indicate that this cation exchange procedure is likely to be useful for quantification of bases. Overall, the recoveries of malonic acid and isobutylamine are important indications that this cation exchange method is capable of separating and recovering both acidic and basic analytes.

3.2.3.2 Amides

Table 5 shows that the matrix-free recoveries of the four amides (OZD, HEIA, HES and BHEOX) all exceeded 150% following derivatisation and acetylation. The matrix-matched recoveries of these compounds were also unacceptable, indicating that dehydration followed by acetylation is not suitable for the analysis of these amides in degraded 30% MEA matrices. However, the matrix-free recoveries of HES, HEIA and OZD following cation exchange and acetylation were within 80-120%, indicating that this may be a suitable sample preparation method for GC-MS analysis of these analytes.

Table 5 shows the impressive improvement in both the matrix-matched and matrix-free recoveries of 2-oxazolidione following derivatisation. This improvement clearly demonstrates the importance of minimizing the interactions between analytes, other SVOCs and non-volatile components during GC-MS analysis. Table 6 shows that 2-oxazolidione was recovered from all three samples of degraded aqueous amine systems within 90-100% , indicating that cation exchange and acetylation are suitable sample preparation procedures for the GC-MS analysis of 2-oxazolidione in these matrices.

Table 6 shows that 1.0 g/kg HES recovery was within 80-120% for all sample and blank matrices with the exception of the sample B. However, the variable and often large %RPDs of the HES concentrations measured in separate subsamples of the samples A, B and C suggest that cation exchange, acetylation and GC-MS may not be suitable for the quantification of HES in these matrices. However, one possible source of this variability is the measurement of HES in both the *acids and neutrals* and *bases* cation exchange fractions. Optimising the cation exchange procedure to ensure the complete elution of HES in one fraction will minimize the error in the GC-MS measurement, and may enable the use of a similar cation exchange, acetylation and GC-MS method for the analysis of HES in degraded 30% MEA samples.

Table 6 shows that the 1.4 g/kg of HEIA added to the blank matrix was measured accurately with matrix-free and matrix-matched recoveries of 100 and 102% respectively. However, the consistently increasing recoveries of HEIA samples A, B and C suggest the presence of a matrix-induced enhancement effect due to matrix components other than water and MEA. The matrix-matched recoveries did not exceed 140%, indicating that HEIA is not as sensitive to this effect as other SVOC such as HEI or DEA. Nevertheless, these results suggests that the presence of a matrix-induced enhancement effect should be investigated prior to the quantification of HEIA by cation exchange, acetylation and GC-MS.

Unlike OZD, HES and HEIA, the matrix-free recoveries of BHEOX added to blank matrices were >150% following both dehydration and cation exchange. This contrasts strongly with the low (<50%) recovery of BHEOX added to the sample B following both dehydration and cation exchange. Table 6 shows that the recovery of BHEOX from all three sample matrices following cation exchange were also very low (<50%). The consistent difference between the recoveries of BHEOX from blank and sample matrices indicates that a matrix component other than MEA or water is preventing the accurate measurement of BHEOX by dehydration or cation exchange with acetylation and GC-MS.

One possible explanation for the wide discrepancy in the recovery of BHEOX from sample and blank matrices is the differences in the alkalinity of the sample matrix. BHEOX is an amide and the relative concentrations of oxamide, N-(2-hydroxyethyl)-2-oxoacetamide (HEO) and N,N-bis(2-hydroxyethyl)oxamide (BHEOX) may be dependent on the alkalinity of the MEA solution. The accumulation of heat stable salts and the presence of CO_2 in degraded aqueous amine systems will decrease the alkalinity (i.e. the proton absorbing capacity of the absorbent) relative to the matrix blank (30% MEA in water).

Overall, these results demonstrate that this cation exchange, acetylation and GC-MS method is suitable for the quantification of OZD but requires further optimization prior to quantification of the other amides. In particular, the cation exchange fractionation needs to be improved to optimize the separation of HES and the matrix-induced enhancement effect needs to be measured prior to the quantification of HEIA. The low recoveries of BHEOX could be due to reduced alkalinity of the degraded MEA samples rather than biases inherent in the cation exchange, acetylation and GC-MS method. The resistance of other amides to changes in alkalinity may be a result of their cyclic structure.

3.2.3.3 HEI

The data in Table 5 indicate that the acetyl derivative of the heteroaromatic degradation product, HEI, added to the blank matrix was not accurately measured following either cation exchange or dehydration. However, the excellent repeatability (RPD <10%) of HEI concentration measurements following cation exchange for all measured concentrations in Table 6 indicates that the use of matrix-induced enhancement factors may enable the use of GC-MS for quantification of the acetyl derivatives of HEI.

Matrix-matched recoveries following both sample preparation procedures were high (>150%, Table 5), indicating that matrix components other than MEA and water also influenced the measurement of HEI concentrations by acetylation and GC-MS. Table 6 also shows that the matrix-free recoveries of 1.1 g/kg HEI added to samples A, B and C consistently increased with the severity of the degradation of the aqueous amine system. Overall the variability of recoveries from both dehydration and cation exchange procedures indicates that neither method is suitable for quantification of HEI without the determination and use of suitable matrix-induced enhancement correction factors.

One possible cause of the consistent overestimation of HEI concentrations following both sample preparation methods is the acetylation procedure. HEI is the only compound analysed in this study with an aromatic heterocyclic system and the derivatisation efficiency of one or more of the nitrogen or oxygen atoms may be dependent on conditions (e.g. presence of trace amounts of water, or concentration of primary amines such as MEA). Furthermore, pyridine (nitrogen containing aromatic heterocycle) is used as a catalyst for the acetylation reaction, indicating that the imidazole system may also interact with the anhydride derivatisation reagent. For this reason, the recoveries of HEI using the cation exchange and GC-MS may be improved by: (a) optimization of the acetylation procedure; (b) the use of an appropriate deuterated surrogate standard; (c) the use of a stronger acetylation reagent (e.g. trifluoroacetic anhydride); or (d) the use of a different derivatisation procedure.

3.2.3.4 Secondary and tertiary amines

Table 5 shows that the matrix-free recoveries of bicine and HEEDA following dehydration and acetylation were >150% and exceeded 70-130% for DEA. Furthermore, 0.31 g/kg HEEDA was not recovered following dehydration and acetylation. Although some of the matrix matched recoveries of these compounds were within 70-130%, dehydration is not recommended for the analysis of these reactive amines. In contrast, Table 5 shows that the recoveries of DEA, bicine and HEEDA from the blank matrix were all within 80-120% following cation exchange and derivatisation. However, none of these secondary or tertiary amines were detected in samples A, B or C following cation exchange and, for this reason; no information about the repeatability of bicine, DEA or HEEDA is given in Table 6.

Table 5 shows that the concentrations of bicine spiked into the matrix blank were accurately measured following cation exchange but the high and variable matrix-matched recoveries of bicine from samples A, B and C listed in Table 6 demonstrate that this cation exchange and acetylation procedure is only suitable for the analysis of bicine in 30% MEA samples that are mildly degraded. The variable recoveries of bicine could be due to the different chemical environments of each degraded sample because, in aqueous solutions, bicine exists in equilibrium with its lactone. However, the excellent matrix-free recovery from the blank matrix but high recoveries from the samples A, B and C suggests that matrix-induced enhancement is a more likely explanation.

The matrix matched recoveries of DEA and HEEDA following cation exchange and acetylation (Table 6) from samples A, B and C increased from 107% to 511% (DEA) or 220% to 750% (HEEDA), despite accurate recovery of these compounds spiked into the matrix blank. This indicates that matrix components other than water and MEA caused a significant matrix-induced enhancement. These results demonstrate that cation exchange and acetylation are not suitable sample preparation procedures for quantification of DEA or HEEDA in these severely degraded aqueous amine systems unless suitable matrix-induced enhancement correction factors are determined and used.

4. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

We have demonstrated for the first time that GC-MS can be used for the quantification of organic degradation products in aqueous MEA absorbents samples from a PCC pilot plant. Both derivatisation and sample cleanup were necessary components of the GC-MS analysis of these analytes in these degraded 30% (w/w) MEA samples. These sample cleanup and derivatisation techniques may also be useful for improving the quantification of organic amine degradation products by alternate analytical instruments such as HPLC and capillary electrophoresis.

The significant reduction in water content enabled the use of BF_3-butanol and acetyl aldehyde, which are both sensitive to water. The derivatisation efficiency of some of the target SVOCs were dependent on reaction conditions, indicating that the derivatisation conditions require further investigation and optimization. Other water-sensitive derivatives, including alkylsilyl derivatives, may also be suitable for the analysis of organic degradation products in aqueous amine systems following the use of appropriate sample preparation techniques.

The cation exchange sample cleanup method was preferred for the analysis of these organic degradation products in these samples. Unlike cation exchange, the dehydration procedure provided opportunities for further sample degradation to occur during the use of heat and vacuum, as well as with the use of highly polar, high surface area molecular sieves. Furthermore, the recovery and repeatability of GC-MS measurements following cation exchange were superior to the GC-MS measurements following dehydration.

Despite the use of cation exchange and derivatisation, some analytes remained difficult to recover reliably from these matrices. Some of these compounds (e.g. bicine and HEI) were most likely subject to matrix-induced enhancement effects or sensitive to derivatisation conditions. Other compounds (e.g. amides) were difficult to recover accurately from the samples and the blank matrix because they exist in equilibrium with other species (e.g. BHEOX, HEO and oxalate).

The excellent agreement between the formic and acetic acids concentrations measured by cation exchange, butylation with GC-MS analysis compared to ion chromatography is a strong indicator that cation exchange is a suitable sample cleanup technique for the analysis or organic degradation products in aqueous amine systems. The accurate recovery of the surrogate standards (malonic acid and isobutylamine) provides further confirmation that the cation exchange, derivatisation and GC-MS method is suitable for the analysis of SVOCs in these samples. The sensitivity, repeatability and accuracy of this GC-MS analytical method could be improved by (a) increasing the scale of the cation exchange and/or derivisation procedures, (b) optimizing the derivatisation reaction conditions and (c) the use of a narrower bore (e.g. 0.25 mmID) GC-MS column. These cation exchange and derivatisation procedures may be useful for quantification of degradation products in other aqueous amine absorbents and, thus, can provide useful insights into the degradation of amine absorbents during PCC of CO_2.

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ABBREVIATIONS

BHEOX, N,N’-bis(2-hydroxethyl)oxamide; DEA, diethanolamine; GC-MS, gas chromatography with mass spectrometry detection; HEA, N-(2-hydroxyethyl)acetamide; HEEDA, 2-(2-hydroxyethylamino)ethanol; HEI, N-(2-hydroxyethyl)imidazole; HEIA, N-(2-hydroxyethyl)-2-imidazolidione; HES, N-(2-hydroxyethyl)succinimide; HSS, heat-stable salts; MEA, monoethanolamine; PCC, post-combustion capture of CO_2; SPE, solid phase extraction; SVOC, semi-volatile organic compounds.

ASSOCIATED CONTENT

The recoveries of all analytes from both sample B and the blank matrix are presented in the supplementary information.

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Supplementary information for Reynolds, A. J., Verheyen, T. V., Adeloju, S. B., Chaffee, A. L., Meuleman, E., 2015, Comparison of sample preparation methods for the GC-MS analysis of monoethanolamine (MEA) degradation products generated during post-combustion capture of CO_2, Energy and Fuels, submitted.

Table SI.1. Measured concentrations, RPDs and recoveries of MEA degradation products using cation exchange, dehydration and acetylation with GC-MS analysis

Method	**Derivative**	**Spiking level**	**HEA**	**Bicine**	**BHEOX**	**HES**	**HEEDA**	**HEI**	**HEIA**	**OZD**	**DEA**
Concentration (g/kg)											
Blank matrix											
SCX	None	NA				<0.1		<0.1	<0.1	0.014	
	AA*	NA			<0.1	<0.1	<0.1	0.06	0.06		
Dehyd.	AA	NA				<0.1	<0.1	0.02	0.02	0.42	
Sample B											
SCX	None	NA	0.54	0.82		0.1		1.3	0.19	1.2	
	AA*	NA			0.29	0.04		0.54	0.18	0.09	
Dehyd.	AA	NA				0.3		0.97	0.19		<0.1
RSD (%)											
Blank Matrix											
SCX	None	NA								123	
	AA*	NA						0.3	12		
Dehyd.	AA	NA						67	12		
Sample B											
SCX	None	NA	8	14		11		0.4	4.1	2.4	
	AA*	NA			12	3		5	8	<1	
Dehyd.	AA	NA				22		14	9.5		
Matrix-free recovery (%)											
Blank matrix											
SCX	None	1	16	166		28		117	27	106	
		2	54			21		112	60	73	
		3				97			180	160	
	AA	4									
Dehyd.	AA	1		260	670	180	220	200	210	260	61
		2		109	350	68	200	310	210	69	25
		3							230		
Sample B											
SCX	None	1	36	370		28		180	24	127	
		2		140		<0		210	66	162	
Dehyd.	AA	1		240		280	200	310	230	320	67
		2		130		71		190	85	58	12
									54		
Matrix-matched recovery (%)											
Sample B											
SCX	None	1	230	220		100		160	92	119	
		2						190	110	220	
Dehyd.	AA	1		106		180	101	180	130	140	57
		2		140		120		75	53	99	124
		3							176		

*n=2. AA, acetyl derivative; BHEOX, N,N'-bis(2-hydroxethyl)oxamide; DEA, diethanolamine; Dehydr. Dehydration sample preparation method; HEA, N-(2-hydroxyethyl)acetamide; HEEDA, 2-(2-hydroxyethylamino)ethanol; HEI, N-(2-hydroxyethyl)imidazole; HEIA, N-(2-hydroxyethyl)-2-imidazolidione; HES, N-(2-hydroxyethyl)succinimide; HSS, heat-stable salts; MEA, monoethanolamine; SCX, strong-cation exchange solid phase extraction sample preparation method; TFAA, trifluoroacetyl derivative.

Chapter 7: Organic degradation products

MEA degradation during pilot scale post-combustion capture of CO_2 from a brown coal-fired power station

Chapter 7 includes a manuscript submitted to the *Energy and Fuels* journal in 2015 for peer review and publication. Chapter 7 relies heavily on the methods, findings and data presented in the previous chapters to achieve all three aims of this thesis. The full citation for the paper in this chapter is:

Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Chaffee, A., Meuleman, E., 2015. MEA degradation during pilot scale post-combustion capture of CO_2 from a brown coal-fired power station. Energy and Fuels, submitted.

Declaration for Thesis Chapter 7

Declaration by candidate

In the case of Chapter 7, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Defined the aims and scope of the manuscript, conducted all the laboratory work, wrote the initial draft of the paper and coordinated feedback and comments from all authors.	80

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
T. Vincent Verheyen	Provided valuable advice on the use and interpretation of data presented in this manuscript. Provided valuable advice on the structure, content and presentation of the manuscript.	N/A
Samuel B. Adeloju	Valuable advice on the structure, content and presentation of the manuscript. Co-ordinated submission and revision of the article	N/A
Erik Meuleman	Provided the sample set and associated pilot plant operation data. Provided valuable comments on the final drafts.	N/A
Alan L. Chaffee	Valuable input into final drafts	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature	A. Reynolds	**Date** 31-Mar-2015
Main Supervisor's Signature		**Date** 31/3/15

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

MEA degradation during pilot scale post-combustion capture of CO_2 from a brown coal-fired power station

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ABSTRACT

One promising technology for mitigating anthropogenic greenhouse gas emissions by post-combustion capture (PCC) of CO_2 involves wet gas scrubbing with aqueous amines. However, the use of aqueous amines, such as MEA (monoethanolamine, 2-aminoethanol), for PCC from fossil-fuel fired power station flue gases leads to undesirable reactions with oxygen, SO_x and NO_x. Extensive study of the chemical degradation of MEA at laboratory scale has demonstrated that the most rapid reaction pathways are oxidative degradation and carbamate polyermisation. The oxidative degradation is usually catalyzed by transition metals, leading to the formation of heat-stable salts (HSS).

This study has used a GC-MS method to measure the changes in concentrations of organic compounds in samples of a 30% (w/w) aqueous MEA absorbent obtained from CSIRO's PCC pilot plant operating at AGL's Loy Yang brown coal-fired power station in Latrobe Valley, Victoria, Australia. This aqueous MEA absorbent was previously used for more than 700 h of PCC and the collected samples represent a further 834 h of PCC operation. No defoamer, anticorrosion or antioxidants were added to this absorbent at any time, despite difficulties maintaining stable operation of the pilot plant.

The alignment of a disturbance in the concentration profiles of the organic degradation products and the rapid increase in iron concentrations measured previously provided a new perspective on the close, interdependent relationships between corrosion and amine degradation reactions. Other important outcomes include confirmation that: (a) organic degradation products identified during laboratory scale trials were also produced during pilot scale PCC; and (b) HEI [N-(2-hydroxyethyl)imidazole] is a suitable molecular marker for oxidative degradation of MEA. This investigation has also highlighted areas that require further research, including: (a) determining the mechanisms of oxidative degradation both in the presence and absence of dissolved transition metals; (b) determining the parameters that limit oxidative degradation during pilot scale PCC; (c) investigating the antioxidative or oxygen scavenging properties of partially oxidised amine absorbents during PCC; and (d) measuring the concentrations of glycine, glycolic acid and other potential organic acids during PCC.

Keywords: monoethanolamine, oxidative degradation, carbamate polymerization, gas chromatography with mass spectrometry detection, cation exchange, acetylation.

1. INTRODUCTION

One important technology for reducing anthropogenic CO_2 emissions from point sources is post-combustion capture (PCC) using aqueous amines. Research into the adaption of this existing technology from natural gas and chemical processing industries to coal-fired power station flue gases is ongoing. Managing amine degradation during PCC of CO_2 with aqueous amines is necessary to minimize the potential environmental

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impact that may arise from atmospheric emissions and liquid waste streams.[1,2] Most of the available information about amine degradation to date has been developed from laboratory scale experiments and very little information about amine degradation at pilot or larger scales of PCC from fossil fuel derived flue gases is available. Therefore, the characterization of amine degradation during pilot scale PCC is urgently needed to guide further development of strategies for minimizing and managing amine degradation.

Monoethanolamine (MEA) is the industrial standard alkanolamine and, for this reason, MEA degradation has been studied extensively.[3,4] The degradation of MEA has recently been reviewed in detail.[3,4] Three main pathways of MEA degradation (oxidative degradation, formation of heat-stable salts and carbamate polymerization) have been identified and studied using various experimental setups.[3,4] Carbamate polymerization is also referred to as thermal degradation because it occurs primarily during thermal desorption of CO_2 and thermal amine reclamation.[5] The reactants, mechanisms, intermediates and products of these three reaction pathways are summarized in Table 1.

Table 1. Summary of degradation mechanisms and products after Gouedard et al.[3]

Reaction pathway and reactants	Proposed mechanisms	Proposed intermediates	Final products
Oxidative degradation			
MEA	e^- abstraction	Formaldehyde	Formate Ammonia
	$H^\bullet$ abstraction from amino N	Formaldehyde	Formate Methylamine
	$H^\bullet$ abstraction from α-amino C	Acetaldehyde	Acetate Ammonia
	$H^\bullet$ abstraction from α-hydroxyl C Hydrolysis of ethanimine	Ethanimine Acetaldehyde	
	$H^\bullet$ abstraction from α-amino C Hydrolysis of 2-iminoethanol	2-iminoethanol 2-hydroxyacetaldehyde	2-hydroxyacetate Ammonia
	e^- abstraction	2-hydroxyacetaldehyde	
	$OH^\bullet$ catalyzed auto-oxidation of MEA	None	Glycine
HEF MEA	Intramolecular cyclisation and condensation; S_N2 addition of MEA	OZD	HEEDA
HEGly	*Intramolecular cyclisation and condensation	None	HEPO
HEHEA	Intramolecular cyclisation and condensation		
MEA HEA	Fe(III) catalyzed hydride abstraction; addition of MEA and HEA		
Thermal degradation/carbamate polymerization			
MEA-carbamate	Intramolecular cyclisation	None	OZD
MEA OZD	S_N2 addition	None	HEEDA
HEEDA	Intramolecular cyclisation and condensation	None	HEIA
MEA MEA-carbamate	Condensation	None	N,N'-bis-(2-hydroxyethyl)urea

*mechanism proposed by da Silva et al.[6]. HEA, N-(2-hydroxyethyl)acetamide; HEEDA, N-(2-hydroxyethyl)ethylenediamine; HEF, N-(2-hydroxyethyl)formamide; HEGly, N-(2-hydroxyethyl)glycine; HEHEA, N-(2-hydroxyethyl)-2-hydroxyacetamide; HEIA, N-(2-hydroxyethyl)imidazolid-2-one; HEPO, 4-(2-hydroxyethyl)piperazin-2-one; OZD, 2-oxazolidione.

Oxidative degradation is the most rapid degradation pathway in the presence of oxygen and the main products of oxidative degradation are organic acids.[3,4] The high concentrations [up to 1.8% (w/w)] of these oxidative degradation products measured in aqueous MEA absorbents used to capture CO_2 from coal combustion flue gases[7] highlights the importance of oxidative degradation for PCC. Table 1 shows that a range of mechanisms have been proposed, however, further research is required to determine which mechanisms actually occur during PCC. Dissolved transition metals are also known to catalyze oxidative degradation.[8-10]

The most rapid oxidative degradation reactions produced organic acids and volatile amines.[3,4] During PCC, the volatile amines are emitted from the top of the absorber, while the organic acids accumulate in the absorbent and condense with aqueous amines, such as MEA to form amides.[3,4,11] Unlike MEA-carbamate, the MEA molecules present in these amides are not regenerated during CO_2 desorption and, for this reason, these amides contribute to the heat-stable salt (HSS) concentration. Organic acids and amides from degradation of MEA have also been measured during PCC of CO_2 at pilot[6,7,12,13] and industrial scales.[14] The most concentrated organic acids are usually acetate and formate,[7,15] suggesting that the most probable oxidative degradation mechanisms are hydrogen radical and/or electron abstraction.

4-(2-hydroxyethyl)piperazin-2-one (HEPO) has also been observed during both laboratory and larger scale MEA degradation. Table 1 shows that three mechanisms for HEPO formation during PCC have been proposed. The simplest and most likely mechanism has been proposed by da Silva et al.,[6] but an explanation is still required for the production of the key intermediate, N-(2-hydroxyethyl)glycine. Interestingly, da Silva et al.[6] noted that HEPO does not form during low temperature (ca. 55°C) oxidative experiments.

Another important oxidative degradation product is N-(2-hydroxyethyl)imidazole (HEI). HEI has been identified extensively during laboratory scale degradation experiments[3] and has been identified in aqueous MEA absorbents during larger scale PCC of CO_2 from coal-fired power station flue gases.[6,13] HEI has also been identified as a potential marker for oxidative degradation because it is easily measured by UV-Vis absorbance (chapter 4).[16] . A few simple but important experiments have demonstrated that HEI is formed in aqueous MEA following the addition of either (a) ammonia, glycolaldehyde and formaldehyde; or (b) oxamic acid and formaldehyde.[17]

Table 1 shows that carbamate polymerization products and mechanisms are fairly well understood. 2-oxazolidione (OZD) is the most commonly reported carbamate polymerization product and is the intramolecular amide of MEA-carbamate. N-(2-hydroxyethyl)imidazolidione (HEIA) has been observed during both laboratory[3] and pilot scale[6,7] degradation of MEA and is believed to be one of the main end products of carbamate polymerization.[6,18] An alternative carbamate polymerization pathway is the addition of MEA and the carbamate of MEA to form N,N'-bis(2-hydroxyethyl)urea. This compound is typically present at low concentrations in laboratory scale degradation products, which is consistent with the slow rate of this dimolecular reaction relative to the intramolecular OZD formation.[6]

Table 2. Summary of MEA degradation products that have been detected in samples in 30% (w/w) aqueous MEA during pilot scale PCC

PCC facility	**PCC pilot plants**			**Industrial CO_2 separation facility**
Flue gas source	**Coal fired power station at Niederaussem, Germany**[7]	**Coal fired power station at Esbjerg, Denmark**[13]	***Coal-fired power stations and propane burner**[6]	**Coal fired power station at Trona, California**[14]
N-(2-hydroxyethyl)-2-hydroxyacetamide		X	X	
Acetate	1.8% (w/w)	X	X	X
HEA		X	X	X
Formate	0.2% (w/w)		X	
HEF		X		X
N-(2-hydroxyethyl)glycine			X	
Oxalate	<0.1% (w/w)		X	
BHEOX		X	X	
HEPO		X	X	X
HEI		X	X	
OZD		X	X	X
HEEDA		ND	X	
HEIA	<0.02% (w/w)	X		X
Other compounds		HEHEAA	HEHEAA, HEO, bicine	HES, HEHEAA

X, compound was detected; ND, the concentration was below the detection limit; HEHEAA, N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide; HEO, 2-(2-hydroxyethylamino)-2-oxoacetic acid. *Coal-fired power stations were located at Esbjerg, Denmark and Longannet, Scotland and the propane burner was located at Trondheim, Norway. #Location of the coal-fired power station was not specified.

Table 2 shows that many of the degradation products produced during laboratory scale degradation trials have been detected during pilot and industrial scale separation of CO_2 using MEA. Some important exceptions include glycine, 2-hydroxyacetate (glycolate) and N,N'-bis-(2-hydroxyethyl)urea. The absence of N,N'-bis-(2-hydroxethyl)urea is consistent with the slow formation observed during laboratory scale trials.[3] However, glycine is a potential precursor for N-(2-hydroxyethyl)glycine and HEEDA.[6] The production of 2-hydroxyacetate and/or glycine could provide important information about probable oxidation mechanisms. Table 2 also highlights the absence of quantitative data regarding the concentrations and/or formation rates of these MEA degradation products during PCC. One key reason for the paucity of data describing the degradation of amines during PCC is the difficulty in quantifying these compounds in the aqueous amine matrices.[19]

Both HPLC-MS (high performance liquid chromatography with mass spectrometry detection) and GC-MS (gas chromatography with mass spectrometry detection) have been used extensively for the quantification of organic degradation products during laboratory and pilot scale studies[4] and method validation studies for both HPLC/MS and GC-MS are available (chapter 6).[20,21] Although HPLC-MS is preferred by some researchers due to its superior sensitivity,[6] the combination of cation exchange, derivatisation and GC-MS analysis is used in this study to facilitate the tentative identification of organic degradation products that were not available as reference standards.

This study aims to characterise MEA degradation during pilot scale PCC and thereby: (a) validate previously established MEA degradation mechanisms and reaction pathways; (b) identify reaction pathways, mechanisms and other physicochemical interactions that are significant for pilot scale PCC; and (c) provide guidance for the minimization of amine degradation during PCC. The organic degradation products were measured in samples of 30% (w/w) aqueous MEA obtained from CSIRO's PCC pilot plant operating at AGL's Loy Yang brown coal-fired power station in Victoria, Australia over a six month period. This absorbent had been used for PCC for more than 700 h prior to commencing this 834 h campaign. No defoamer, anticorrosion or antioxidant chemicals were added to this absorbent at any time, despite the need to reduce the liquid flow rate to manage increasing pressure drops across the absorber column system.

2. MATERIALS AND METHODS

2.1 Sample set

The sample set used in this investigation has been described in detail in chapter 1 and elsewhere.[16,22,23] In summary, a set of twelve samples of 30% (w/w) aqueous MEA were obtained from CSIRO's PCC pilot plant during a campaign at AGL's Loy Yang brown coal-fired power station in Victoria, Australia. The MEA absorbent was used for pilot scale PCC campaigns at Stanwell's Tarong black-coal fired power station and stored in an intermediate bulk container (IBC) for 18 months prior to the PCC campaign at Loy Yang. Samples of cold, lean aqueous MEA were taken downstream of a balance tank, collected in acid-washed HDPE sample containers, transferred immediately to the laboratory and stored in the dark at -20°C. An additional sample of absorbent was obtained directly from the IBC prior to the commencement of this campaign, and treated in the same manner as each of the twelve samples taken from the pilot plant. However, the data from this additional sample are not included in the figures or tables unless specified. Details of a concurrent pilot plant campaign are described by Azzi et al.[24]

2.2 Ion chromatography

Acetate, formate and oxalate were quantified as described in chapter 5.[23] Glycolate, acetate and formate were also independently identified and quantified by the analysis of three samples using a Metrohm 930 IC Flex with sequential suppression, Metrosep ASUPP7 (25 mm, 4µm) column and a Metrosep RP2 guard column.

2.3 Heat-stable salts

The heat-stable salt concentrations were measured by cation exchange and acid-base titration as described in chapter 3.[16]

2.4 GC-MS analysis

The solid phase extraction, derivatisation and GC-MS procedures have been described in detail in chapter 6.[21] In summary, 50 mg of each sample was separated into two fractions (the *acids and neutrals fraction* and the *bases fraction*) using strong cation exchange cartridges (DSC-SCX, 500 mg, 3 mL from Sigma Aldrich, Australia). An aliquot of each *acids and neutrals fraction* was derivatised with 15% BF_3 in n-butanol to convert organic acids to their butyl esters. Aliquots of both fractions (*acids and neutrals* as well as *bases*) were methylated with diazomethane and acetylated with 1:1 acetic anhydride:pyridine. The butyl esters and methyl/acetyl derivatives were analysed using a Varian 3800 GC and Varian Saturn 2200 ion-trap MS. The samples were injected using a 8400 autosampler into a 1177 injector with a deactivated focus liner from SGE (Australia). The GC column was a CP-Sil 8 CB for Amines 30 m × 0.32 mm × 1.0 µm from Agilent (Netherlands).

Reference compounds for the species listed in Table 3 were available in our laboratory and the concentrations of these compounds were calculated using an internal standard calibration. The precision and accuracy of this approach is discussed in detail in chapter 6.[21] The compounds listed in Tables 4 and 5 are tentative identities and pure standards of these compounds were not available in our laboratory. The indicative concentrations of these tentatively identified compounds were estimated from the ratio of the unknown peak area to the internal standard peak area. For this reason, we discuss changes in the ratios of organic degradation products but do not comment on their absolute concentrations.

2.5 Statistical methods

Principal component analysis (PCA) and Kendall's τ coefficient calculations were conducted using IBM SPSS Statistics 20.0.0. PCA was used to group compounds with similar concentration profiles and all compound concentrations were standardized prior to analysis. The varimax algorithm was used maximize the differences between the calculated components. All error bars and uncertainty intervals are the mean deviation of triplicate measurements.

3. RESULTS AND DISCUSSION

3.1 Repeatability of GC-MS analyses

The repeatability and accuracy of this GC-MS method for the compounds listed in Table 3 have been discussed in detail in chapter 6.[21] The relative percent difference (RPD) of concentrations of both target compounds and tentatively identified compounds were calculated from the triplicate injections of each sample and were usually less than 10%. The only RPDs greater than 20% were: (a) RPD<21% for N-(2-hydroxyethyl)succinimide; (b) RPD<21% for the sum of mono- and bisacetyl derivatives of N-(2-hydroxyethyl)imidazolidione; and (c) RPD<22% for the sum of 2-oxazolidione and the acetyl derivative of 2-oxazolidione. These RPDs indicate that the GC-MS analyses of the derivatised extracts were reproducible.

Three samples (the first, middle and last) were extracted, derivatised and analysed in duplicate. Many of the tentatively identified compounds were present at very low concentrations in the first sample and for this reason, the RPD of concentrations calculated from duplicate analyses of the first sample were often greater than 20%. The only RPDs greater than 20% for the middle and last sample were: (a) RPD<21% for unknown **X** (see Tables 4 and 5 for tentative identification); (b) RPD<29% for **VII**; and (c) RPD<59% for **XII**. With the possible exception of **XII**, these RPDs indicate that the extraction and derivatisation procedures are suitable for the analysis of these tentatively identified compounds. In the absence of pure standards, the precision of the extraction, derivatisation and GC-MS method for the analysis of the tentatively identified compounds could not be determined.

3.2 Tentative identification of organic degradation products

3.2.1 SPE, derivatisation and mass spectral characteristics of reference compounds

The relationships between the cation exchange fraction, retention time, mass spectra, $[M+1]^+$ ion assignments and common neutral loss fragments of the reference compounds are listed in Table 3. These parameters show that important structural information was generated from each stage of the SPE, derivatisation and GC-MS analysis. This information was then used to propose tentative identifications for the compounds listed in Tables 4 and 5.

The separation of the reference compounds listed in Table 3 into two fractions by cation exchange has been discussed in chapter 6.[21] In summary, the free organic acids eluted in the acids and neutrals fraction; alkanolamines (MEA and DEA) and amines (HEI and HEEDA) eluted in the bases fraction; and linear or cyclic amides eluted either in the *acids and neutrals* fraction (2-oxazolidione and BHEOX) or both fractions (HEIA and HES). Interestingly, bicine (which has both organic acid and tertiary amine functional groups) eluted completely in the *bases* fraction. This indicates that a compound containing an ionisable amino functional group is likely to be retained by the strong cation exchange resin and elute in the *bases* fraction, regardless of the presence of carboxylic or other acidic functional groups.

The GC-MS data confirmed that methylation with diazomethane converted all the free acids to methyl esters and all of the hydroxyl and free amine groups of the known degradation products were completely derivatised by acetic anhydride. Amides were not usually acetylated, although the amide nitrogen atoms of OZD and HEIA were partially acetylated. The partial acetylation of the OZD and HEIA amide nitrogen atoms is possibly a result of the resonance between the amide and amine structures of these nitrogen atoms. Further evidence for mixed amine and amide behavior of the secondary nitrogen in HEIA is provided by the partial retention of HEIA by the cation exchange resin during SPE and elution of HEIA in both fractions.

One important characteristic of the mass spectra for the target organic degradation products listed in Table 3 is the frequent presence of the $[M+1]^+$ ion. The protonation of the molecular ion is likely to be due to chemical reactions in the ion trap mass spectrometer used in this study. The $[M+1]^+$ ion was observed for all target organic degradation products except bicine, BHEOX, HEEDA and the bisacetyl derivative of HEIA. It is likely that BHEOX and the bisacetyl derivative of HEIA both formed stable conjugated fragments in preference to the molecular ion. Bicine, HEEDA and BHEOX contained secondary amine and/or two hydroxyethyl substituents and the acetyl derivatives of these groups are able to form stable neutral fragments that are likely to be cleaved from the molecular ion. The absence of the $[M+1]^+$ ion in some mass spectra of the target organic degradation products highlights the difficulty of assigning a $[M+1]^+$ mass in the absence of a reference compounds. However, the GC retention times provided critical information about the probable vapor pressures and molecular masses of each organic compound and assisted in the tentative assignment of $[M+1]^+$ ions.

The mass spectra of the reference compounds in Table 3 also contain a number of characteristic fragments and neutral losses. The common MS fragments in Figure 1 are also observed in the mass spectra of most of the tentatively identified organic degradation products listed in Tables 4 and 5. These fragments indicate the presence of 2-hydroxyethyl or secondary 2-aminohydroxyethyl substituents; however, they do not provide comprehensive structural information.

The MS fragments shown in Figure 2 were all generated by loss of neutral fragments shown in Figure 3. Many of these fragments are likely to be stabilized by conjugation and/or cyclisation. Importantly, all of these fragments provide important information about the structure of the parent compound. Furthermore, many of the fragments observed in the mass spectra of the unknown organic degradation products in Tables 4 and 5 can be explained by the same neutral loss fragments shown in Figure 3.

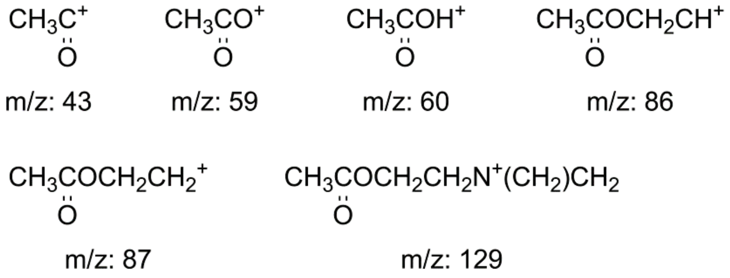
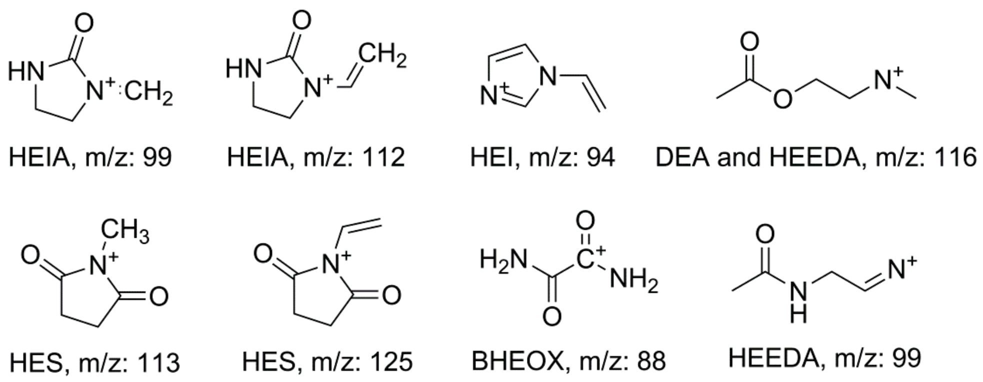


Figure 1. Proposed structures of common fragments generated from MEA degradation products by 70 eV ionization

Table 3. Mass spectra, SPE fractionation and concentration range of the organic MEA degradation products confirmed by reference standards

Parent structure	**SPE fraction**	**Molecular mass of parent structure**	**Molecular mass derivative[#]**	**Mass spectra**	**Concentration range (g/kg)**
2-oxazolidione (OZD)	Acid and neutrals	87	---*	88 (100)	0.085(1) - 0.35(3)
			129	42(19) 43(67) 56(11) 88(17) 101(100) 129(26) 130(18)	
Monoethanolamine (MEA)	Bases	61	145	43(100) 44(13) 60(12) 85(19) 86(92) 102(12) 146(29)	
N-(2-hydroxyethyl)imidazole (HEI)	Bases	112	154	40(11) 41(13) 42(11) 43(80) 54(18) 67(30) 81(37) 82(16) 87(20) 93(11) 94(100) 95(10) 154(34) 155(52)	0.38(3) - 2.03(5)
N-(2-hydroxyethyl)succinimide (HES)	Both	143	185	43(19) 43(100) 44(10) 55(33) 56(14) 69(10) 84(50) 85(14) 100(47) 112(17) 113(71) 124(14) 125(100) 126(28) 142(54) 186(30)	0.023(2) - 0.72(2)
Bicine	Bases	163	261	42(16) 43(20) 55(10) 56(34) 86(100) 87(18) 114(48) 127(30) 128(10)	0.164(1) - 0.27(1)
N-(2-hydroxyethyl)-2-imidazolidione (HEIA)	Both	130	172^	42(11) 43(17) 56(46) 99(34) 112(100) 113(17) 172(33)	0.277(2) - 0.96(3)
			214^	43(32) 56(21) 99(100) 112(62) 141(13)	
Diethanolamine (DEA)	Bases	105	231	43(34) 56(13) 74(14) 86(11) 87(95) 116(100) 129(11) 232(15)	ND
2-(2-hydroxyethylamino)ethanol (HEEDA)	Bases	104	230	42(11) 43(18) 44(16) 56(33) 99(100) 112(82) 113(10)	ND
N,N'-bis(2-hydroxyethyl)oxamide (BHEOX)	Acid and neutrals	176	260	42(23) 43(100) 44(25) 88(65) 115(13)	0.43(1) - 3.41(6)

[#]Methyl-acetyl derivatives; *OZD was only partially derivatised; ^the amide N of HEIA was only partially derivatised. ND, not detected.

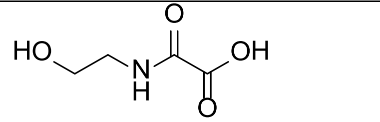
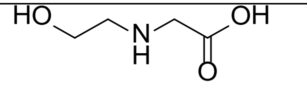
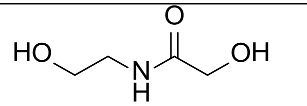
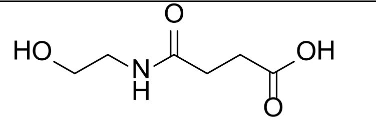
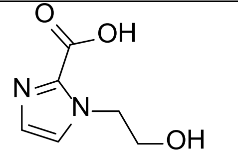
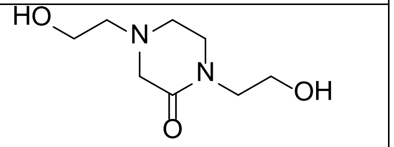
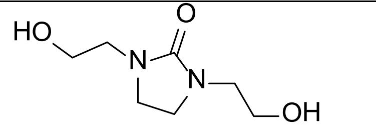


HEIA, m/z: 99 HEIA, m/z: 112 HEI, m/z: 94 DEA and HEEDA, m/z: 116

HES, m/z: 113 HES, m/z: 125 BHEOX, m/z: 88 HEEDA, m/z: 99

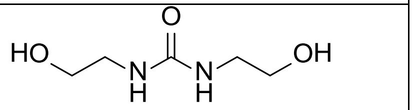
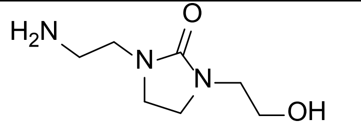
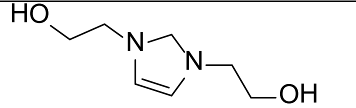
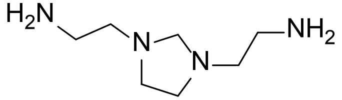
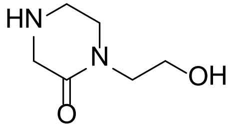
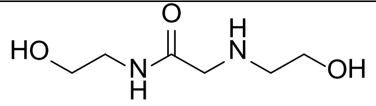
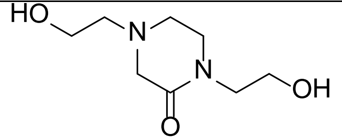
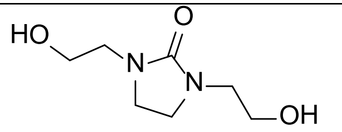
Figure 2. Proposed structures of the 70eV fragments that were characteristic for the acetyl derivatives of compound standards

Table 4. GC-MS retention time, mass spectra and tentative identifications of unknown organic degradation products that eluted in the *acids and neutrals* SPE fractions

ID	**T_r (min)**	**Mass spectrum**	**Proposed fragment structures**	**Tentative identification**	**Mr ***	**Compound structure**
I	11.6	44(19) 130(38) 189(19) 190(100)	130 m/z: M^+-59, M-$CH_3C(O)O$	2-(2-hydroxyethylamino)-2-oxoacetic acid	133, 189	
II	12.1	42(13) 43(100) 44(13) 88(44) 97(17) 115(17) 218(22)	115 m/z: M^+-43-59, M^+-CH_3OC-$CH_3C(O)O$ 158 m/z: M^+-59, M^+-$CH_3C(O)O$	N-(2-hydroxyethyl)glycine	119, 217	
IV	12.2	42(16) 43(100) 44(16) 83(13) 101(54) 144(26) 204(52)	101 m/z: M^+-43-59, M^+-CH_3CO-$CH_3C(O)O$ 144 m/z: M^+-59, M^+-$CH_3C(O)O$	2-hydroxy-N-(2-hydroxyethyl)acetamide (HHEA)	119, 203	
V	13.5	43(17) 55(13) 87(15) 114(11) 115(100) 126(12) 218(75)	115 m/z: M^+-102, M^+-43-59, M^+-CH_3CO-$CH_3C(O)O$	N-(2-hydroxyethyl)succinamide	161, 217	
VII	15.7	43(26) 43 (100) 44(34) 87(12) 88(40) 115(18)		Amide		
VIII	15.8	42(12) 43(48) 56(84) 69(15) 70(16) 87(100) 114(12) 149(21)		Amide		
X	15.9	42(84) 43(98) 55(13) 56(26) 87(100) 100(21) 127(16) 128(10) 140(15) 152(74)	152 m/z: M^+-60, M^+-$CH_3C(O)OCH_3$	1-(2-hydroxyethyl)-1H-imidazole-2-carboxylic acid	156, 212	
XII	16.6	42(29) 43(71) 44(15) 56(55) 57(13) 60(14) 74(45) 85(29) 87(100) 88(12) 113(24) 116(53)		Amide		
XVI	17.4	42(33) 43(78) 56(90) 69(14) 70(21) 87(100) 88(11) 111(10) 116(10) 130(32) 137(13) 139(20) 142(41) 154(12)	130 m/z: M^+-142, 272-28-114, 272-CO-$CH_3C(O)OCH_2CH_2NCH$ 142 m/z: M^+-130, M^+-$CH_3C(O)CH_2CH_2NCH_2CH_3$ 154 m/z: M^+-118, M^+-59-59, M^+-$CH_3C(O)O$-$CH_3C(O)O$	N,N'-bis-(2-hydroxyethyl)piperazin-2-one	188, 272	
XVII	17.5	42(95) 43(100) 55(15) 56(46) 74(14) 87(78) 97(18) 98(34) 99(14) 116(63) 125(17) 138(14) 139(23) 140(59) 141(57) 143(15)	140 m/z: M^+-73-44, M^+-$CH_3C(O)OCH_2$-$CH_3C(O)H$ 141 m/z: M^+-73-43, M^+-$CH_3C(O)OCH_2$-$CH_3C(O)$ 185 m/z: M^+-73, M^+-$CH_3C(O)OCH_2$	N,N'-bis-(2-hydroxyethyl)imidazolidione	174, 258	

*parent compound, methyl-acetyl derivative

Table 5. GC-MS retention time, mass spectra and tentative identifications of unknown organic degradation products that eluted in the *bases* SPE fractions

ID	T_r (min)	Mass spectrum	Proposed fragment structures	Tentative identification	M_r*	Compound structure
III	12.1	42(25) 55(15) 56(88) 57(83) 58(19) 70(17) 71(36) 72(15) 99(17) 100(16) 101(48) 102(27) 143(26) 144(75) 157(20) 158(100)		Small amine	157	
VI	15.2	42(27) 43(100) 44(19) 87(17) 88(21) 112(22) 130(18) 233(26)	112 m/z: M^+-60-60, M^+-$CH_3C(O)OH$-$CH_3C(O)OH$ 130 m/z: M^+-43-59, M^+-CH_3CO-$CH_3C(O)O$	N,N'-bis(2-hydroxyethyl)urea	148, 232	
IX	15.8	42(26) 43(10) 56(17) 87(100) 98(26) 116(15) 185(51)	185 m/z: M^+-72, M^+-$CH_3C(O)NHCH2$	N-(2-aminoethyl)-N’-(2-hydroxyethyl)imidazolidione (AEHEIA)	173, 257	
XI	16.3	42(34) 56(20) 86(16) 87(62) 98(23) 99(11) 125(13) 127(12) 153(56) 154(11) 166(90) 167(11) 185(100) 229(13) 243(23)	153 m/z: M^+-73-16, M^+-$CH_3C(O)OCH_2$-CH_4 166 m/z: M^+-60-16, M^+- $CH_3C(O)OH$-CH_4 185 m/z: M^+-42-15, M^+-$CH_2C(O)O$-CH_3	N,N’-bis-(2-hydroxyethyl)2,3-dihydro-1H-imidazole or N,N’-bis(2-aminoethyl)-imidazolidione	158, 242	 
XIII	16.8	70(11) 87(100) 112(19) 128(11) 130(84) 131(11) 172(11) 199(14) 200(39) 201(11) 229(15)	200 m/z: M^+-28, M^+-C=O 130 m/z: M^+-28-70: M^+-CO- $CH_2C(O)O$	HEPO	144, 228	
XIV	16.8	87(100) 99(11) 113(24)	113 m/z: M^+-73-59-43, M^+- $CH_3C(O)OCH_2$-CH_3CO-$CH_3C(O)O$ 116 m/z: M^+-129-43, M^+-$CH_3C(O)OCH_2CH_2NC(O)$-CH_2CO 186 m/z: M^+-59-43, M^+-CH_3CO-$CH_3C(O)O$	HEHEA	162, 288	
XV	17.1	56(20) 70(12) 86(100) 114(50)		Amine, MEA oligomer		
XVI	17.4	42(33) 43(78) 56(90) 69(14) 70(21) 87(100) 88(11) 111(10) 116(10) 130(32) 137(13) 139(20) 142(41) 154(12)	130 m/z: M^+-142, 272-28-114, 272-CO-$CH_3C(O)OCH_2CH_2NCH$ 142 m/z: M^+-130, M^+-$CH_3C(O)CH_2CH_2NCH_2CH_3$ 154 m/z: M^+-118, M^+-59-59, M^+-$CH_3C(O)O$-$CH_3C(O)O$	N,N’-bis-(2-hydroxyethyl)piperazin-2-one	188, 272	
XVII	17.5	42(95) 43(100) 55(15) 56(46) 74(14) 87(78) 97(18) 98(34) 99(14) 116(63) 125(17) 138(14) 139(23) 140(59) 141(57) 143(15)	140 m/z: M^+-73-44, M^+-$CH_3C(O)OCH_2$-$CH_3C(O)H$ 141 m/z: M^+-73-43, M^+-$CH_3C(O)OCH_2$-$CH_3C(O)$ 185 m/z: M^+-73, M^+-$CH_3C(O)OCH_2$	N,N’-bis-(2-hydroxyethyl)imidazolidione	174, 258	
XVIII	21.1	42(12) 43(55) 56(10) 87(100) 116(35) 130(18)		Amine, MEA oligomer		

*parent compound, methyl-acetyl derivative

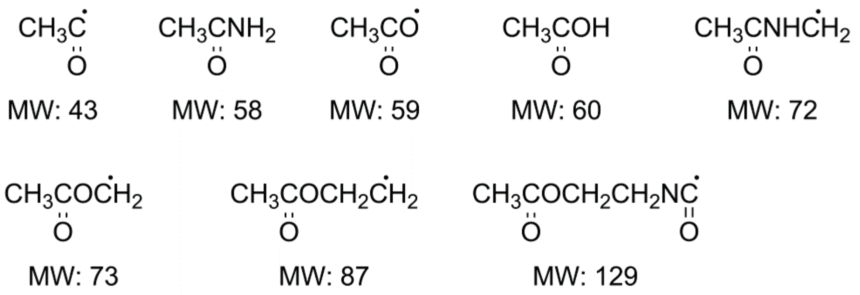


Figure 3. Neutral fragments commonly lost after 70eV ionization of acetyl derivatives

3.2.2 Organic acids

Organic acids were present in the degraded MEA as both free organic acid anions and as amides of MEA. The concentrations of formate, acetate and oxalate were determined by ion chromatography, but GC-MS was also used to identify organic acids following cation exchange and butylation. N-(2-hydroxyethyl)formamide (HEF) and N-(2-hydroxyethyl)acetamide (HEA) were not detected after acetylation because: (i) the acetyl derivative of HEA is identical to the acetyl derivative MEA; and (ii) HEF was not reliably resolved from the acetyl derivative of MEA. However, N,N'-bis-(2-hydroxyethyl)oxamide (BHEOX) is included in Table 3 and was quantified by GC-MS as the acetyl derivative.

Glycolate and succinate were also identified in these samples, but were not quantified or included in the statistical analyses. Glycolate was not quantified in this study because (i) glycolate was not resolved from acetate by ion chromatography and (ii) the glycolate ester peak tailed severely during the GC-MS analysis of sample extracts. The butyl ester of succinate was tentatively identified (but not quantified) from its mass spectrum and retention time in the *acids and neutrals* fractions of all samples following butylation and GC-MS analysis. The presence of other organic acids (e.g. succinate) is also supported by the presence of unidentified peaks in the ion chromatography.

3.2.3 Cyclic organic degradation products: OZD, HEI, HEIA and HES

With the exception of the bisacetyl derivative of HEIA, the $[M+1]^+$ ion was present in the mass spectra of the acetyl derivatives of the alicyclic MEA degradation products, OZD, HEIA and HES. Potential structures of the most stable MS fragments from each of the alicyclic OZD, HEIA and HES derivatives are shown in Figure 2 and all contain the ring structure from the parent compounds. The mass spectrum of the aromatic organic degradation product, HEI, also contained the $[M+1]^+$ fragment and the base peak (94 m/z) contained the aromatic ring of the parent compound. This 94 m/z fragment was probably stabilized by conjugation and rearrangement of the heterocyclic ring and a possible structure is shown in Figure 2.

XIII and **XVI** eluted at 16.8 and 17.4 min, respectively, and produced similar mass spectra. The potential $[M+1]^+$ ion at 229 m/z for **XIII** was consistent with the GC-MS retention time. The molecular mass of the bisacetylated derivatives of the N-(2-hydroxyethyl)piperazinone isomers are 228 amu, giving an $[M+1]^+$ ion of 229 m/z. The base peak of **XIII** is 87 m/z (indicating the presence of an acetylated 2-hydroxyethyl substituent) but the other stable fragment, 130 m/z, is more difficult to account for. The presence of 200 m/z indicates that neutral CO was readily lost from the molecular ion (228 m/z). The loss of CO could leave a linear fragment behind, which could easily lose the stable 60 amu fragment, as shown in Figure 4. The remaining 130 m/z fragment is likely to contain a secondary amine and could recyclise to form a stable, positively charged fragment. For these reasons, **XIII** is tentatively assigned as a N-(2-hydroxethyl)piperazinone isomer. The absence of this compound in the *acids and neutrals* fraction indicates that the isomer is N-(2-hydroxyethyl)piperazin-2-one, which contains a secondary amine instead of an amide nitrogen.

The 130 m/z fragment was also observed in the **XVI** mass spectrum. **XVI** was only present in the *acids and neutrals* fraction and eluted after **XIII**. These observations suggest **XVI** was structurally similar to **XIII**, but did not contain a basic amine. For these reasons, **XVI** is tentatively identified as N-(2-hydroxyethyl)piperazin-2-one (HEPO).

The HEIA characteristic fragments (99 m/z and 112 m/z) were not observed in any other unknown mass spectra in Tables 4 or 5. However, both **IX** and **XVII** contained 98 m/z or 99 m/z as well as 116 m/z. DEA also produced a stable 116 m/z fragment and a similar fragment could easily be produced from an N,N'-bis substituted imidazolidione following loss of CO and ring opening. This is similar to the proposed fragmentation of the piperazinone compounds in Figure 4. The SPE fractionation indicated that **IX** contained a basic amine group, but **XVII** did not contain a basic amine group. For these reasons, **XVII** is tentatively identified as N,N'-bis-(2-hydroxyethyl)imidazolidione and **IX** is tentatively identified as AEHEIA (N-(2-aminoethyl)-N'-(2-hydroxyethyl)imdiazolidione).The remaining MS fragments of **IX** and **XVII** are likely to be produced by loss of the neutral fragments shown in Figure 3.

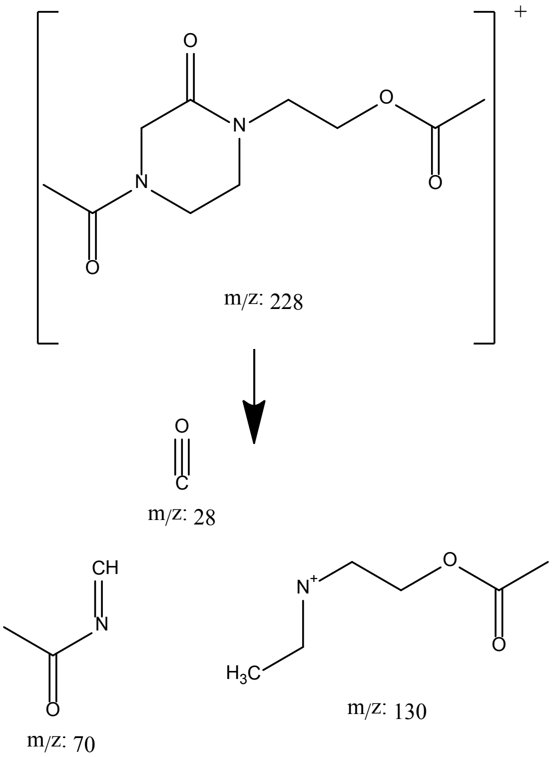


Figure 4. Proposed fragmentation of piperazinone analogues

The mass spectrum of **XI** contained a small $[M+1]^+$ ion at 243 m/z, indicating that the acetyl derivative of **XI** was likely to have a molecular mass of 242 amu. The mass spectrum of **X** was similar to **XI**, but did not contain a potential $[M+1]^+$ ion. These mass spectra of these derivatives contained 98, 99 or 100 m/z, 125 and/or 127 m/z. However, unlike many of the spectra previously considered, the larger fragments of these mass spectra (185 m/z for **XI** and 152 m/z for **X**) were stable. The cation exchange fractionation indicated that **XI** contained a basic amine group, but **X** did not contain a basic amine group.

The molecular mass (242 amu) of the **XI** acetyl derivative suggests that N,N'-bis(2-hydroxyethyl)-2,3-dihydro-1H-imidazole or N,N'-bis(2-aminoethyl)-imidazolidione are probable structures. The stable 185 m/z fragment could be formed from the loss of 57 m/z (possibly a $CH_3C(O)N$ fragment) from the molecular ion. The presence of **XI** in the *bases* fraction also favors the tentative identification of **XI** as N,N'-bis(2-aminoethyl)-imidazolidione. However, this compound has not been previously identified during degradation of MEA.

The mass spectrum of the **X** derivative contained an intense 152 m/z peak, but no potential $[M+1]^+$. The 152 m/z fragment could be formed by the loss of 60 m/z from a 212 amu parent derivative, suggesting that one possible identity is a HEI derivative described previously.[17]

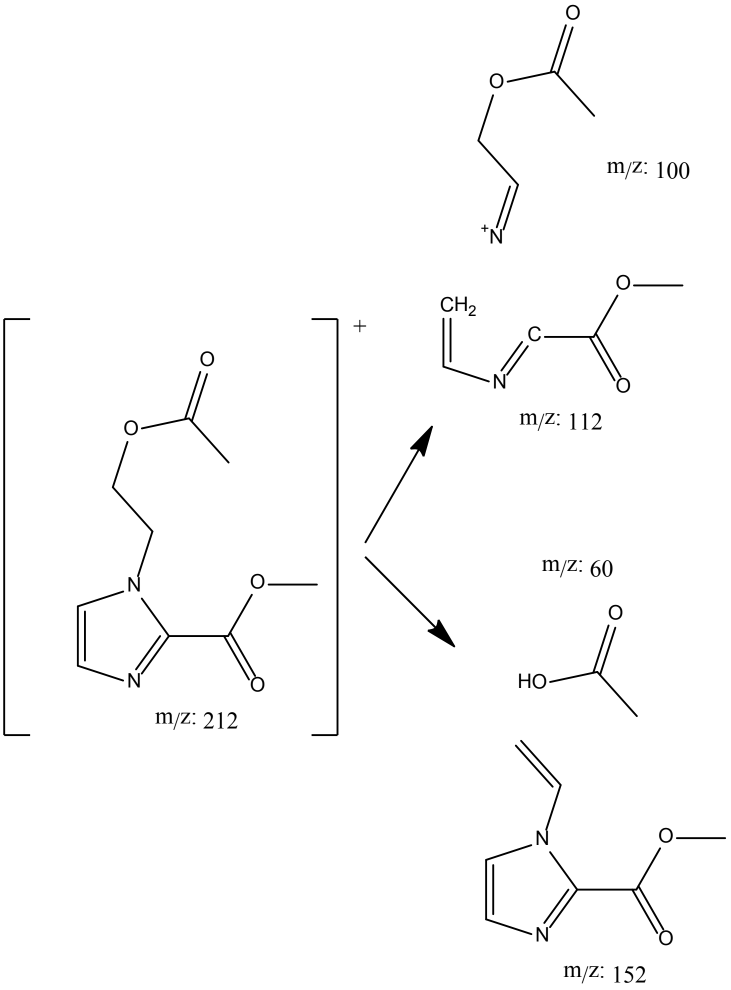


Figure 5. Possible fragmentation of the acetyl derivative of **X**

3.2.4 Alkanolamines and non-cyclic organic degradation products: MEA, DEA, bicine, BHEOX and HEEDA

The acetyl derivatives of the MEA and DEA produced mass spectra containing the $[M+1]^+$ ion in addition to common hydroxyethyl fragments including 43 m/z and 86 or 87 m/z. The base peak of the DEA spectrum was 116 m/z and a proposed structure for this fragment is shown in Figure 2. This fragment was also produced by HEEDA, suggesting that 116 m/z is indicative of the presence of a secondary ethanolamine acetyl derivative. The 116 m/z fragment was also observed in some of the mass spectra listed in Tables 4 and 5.

The mass spectra of bicine, BHEOX and HEEDA all contained few fragments larger than 129 m/z. The mass spectra of five unknown tentatively identified degradation products in Tables 4 and 5 (**VII**, **VIII**, **XII**, **XV**, and **XVIII**) were also dominated by small (<129 m/z) fragments despite GC-MS retention times greater than the acetyl derivative of OZD (M_r=130 amu). **XV** and **XVIII** eluted in the *bases* fraction and, for this reason, these compounds are likely to contain at least one free amine functional group. In contrast, the three compounds that eluted in the *acids and neutrals* fraction (**VII**, **XII** and **VIII**) are likely to contain amide groups, but are unlikely to contain basic amino groups. However, the mass spectra of the acetyl derivatives of these compounds did not contain molecular ions and, for this reason, these amides cannot be confidently identified. One potential amide is N,N'-bis-(2-hydroxyethyl)succinamide which has been identified during laboratory scale experiments.[3] The identification of the other organic acids present in the ion chromatography data would assist identification of other amides.

XV eluted in the *bases* fraction and the mass spectrum of its derivative contained the 114 m/z fragment. The mass spectra of the bicine derivative also contained 114 m/z, indicating that **XV** is likely to be structurally similar to bicine. The retention time of **XV** was 17.1 min, which is significantly longer than bicine (12.6 min) and other compounds with two MEA substituents. For this reason, **XV** is tentatively assigned to the MEA amide of bicine shown in Tables 4 and 5. This tentative assignment is supported by the presence of a 245 m/z fragment at less than 10% of the base peak intensity. This fragment could be formed by the loss of a $CH_3C(O)OCH_2CH_2$ (87 amu) neutral fragment from the methyl/acetyl derivative of **XV**.

XVIII also eluted in the *bases* fraction, but the mass spectrum of the derivative contained the 116 m/z fragment. This fragment was also observed in DEA, indicating that **XVIII** is likely to be structurally similar to DEA. **XVIII** eluted at 21.1 min, indicating that it contained the equivalent of at least three, possibly four, MEA substituents. However, in the absence of further mass spectral details (such as the molecular ion) no tentative identification is given for this compound.

3.2.5 Other tentatively identified compounds

Four compounds in the acids and neutrals fractions eluted between 11.6 and 13.5 min (**I**, **II**, **IV** and **V**). The mass spectra of the derivatives of these compounds all contained probable $[M+1]^+$ ions and the remaining fragments could be produced by loss of the neutral fragments in Figure 3. These compounds were all tentatively identified as amides and are shown in Tables 4 and 5.

The mass spectrum of the smallest derivative eluting in the *bases* fraction (**III**, 12.1 min) produced a stable $[M+1]^+$ ions, indicating that it was likely to have a molecular mass of 157 amu, and may contain an aromatic ring. This compound is not likely to be a contaminant because it was not present in the reagent blanks. However, no tentative identification is assigned to this compound.

The final two compounds (**XIV** and **VI**) listed in Table 5 eluted in the *bases* fraction and were tentatively identified as N,N'-bis-(2-hydroxyethyl)urea and HEHEAA. The acetyl derivative of **VI** eluted at 15.2 min and produced a 233 m/z $[M+1]^+$ ion, suggesting that the 232 amu N,N'-bis(2-hydroxyethyl)urea as a probable identity. The 130 m/z is likely to result from the loss of 43 m/z and 59 m/z fragments, which is consistent with the presence of at least one terminal hydroxyl group. The 112 m/z fragment could result from the loss of two 60 amu fragments, leaving the 112 m/z fragment stabilized by conjugation. The acetyl derivative of **XIV** eluted at 16.8 min and its mass spectrum also contained a small $[M+1]^+$ peak at 289 m/z. The base peak of this mass spectrum was 87 m/z but 99 m/z and 113 m/z were also produced. For these reasons, this compound has been tentatively identified as N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide (HEHEAA), which has a molecular mass of 288 m/z after acetylation.

3.3 Trends

The monotonic increasing trend of HSS and organic acids (acetate, formate and oxalate) during this pilot PCC campaign has been demonstrated previously (chapter 5).[23] The presence of glycolate was also confirmed, indicating that all the proposed mechanisms for formation of organic acids during PCC in Table 1 may have been active during this pilot campaign.

Figure 6 (top) shows that the formate concentrations were higher and increased much more rapidly than oxalate or acetate concentrations. Figure 6 (bottom) shows that the HSS contribution from formate increased from less than 40% to more than 70% during the PCC campaign. Acetate and oxalate concentrations also increased, but their contribution to the HSS did not exceed 30% on an acid equivalent basis. In contrast, during a pilot scale PCC campaign at Esbjerg using 30% (w/w) MEA, the acetate concentrations were significantly higher than the formate concentrations, and acetate was produced more rapidly than formate.[7] Provided the same analytical techniques were used (i.e. ion chromatography), the presence of different ratios of organic acids produced during in different pilot PCC campaigns strongly suggests that different reaction mechanisms dominated during these two pilot PCC campaigns.

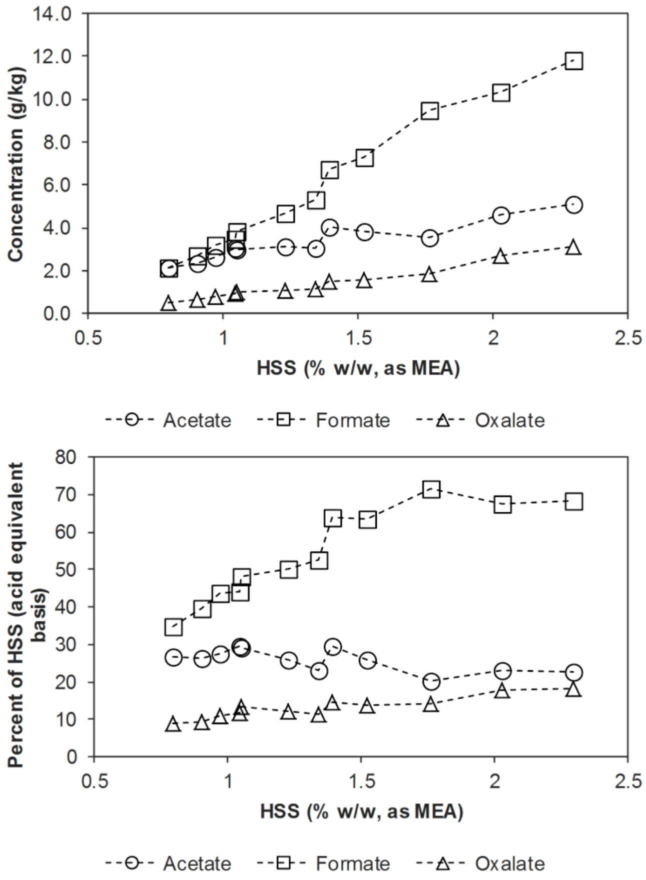


Figure 6. Concentrations of organic acids in the 30% (w/w) aqueous MEA absorbent during pilot scale PCC at Loy Yang

One notable difference between the pilot plant campaigns at Esbjerg and Loy Yang is the concentrations of iron, which is known to catalyse oxidative degradation.[3] The iron concentration in the 30% (w/w) MEA absorbent at Esbjerg remained below 40 mg/kg,[7] but increased up to 199 mg/kg at Loy Yang.[23] Other factors that are likely to influence the kinetic rates of different oxidative degradation mechanisms include operating temperatures of the absorber, desorber and heat exchangers, oxygen concentrations of the flue gas, concentrations of SO_x and accumulation of other potentially catalytic materials such as fly ash. Overall, this difference in oxidative degradation products suggests that PCC operating parameters do influence the rates of different oxidative degradation mechanisms. This illustrates the need to determine the mechanisms of oxidative degradation, conditions that promote or retard oxidative degradation and ultimately, develop effective strategies for minimizing oxidative degradation during PCC.

In contrast to the organic acid concentrations, the Kendall's τ statistics for all of the GC-MS analytes were less than one, indicating that the concentrations of each compound decreased between sampling events at least once. Three GC-MS analytes (HEI, **XI** and **XVIII**) were more than 99% likely to monotonically increase (Kendall's τ>0.7) during this pilot PCC campaign. A further five GC-MS analytes (**I**, **III**, **V**, **XII** and **XVII**) were more than 95% likely to monotonically increase (Kendall's τ>0.5). Four of these compounds were tentatively identified as amides and **XVII** was assigned to a cyclic structure. The changes in the concentrations of these compounds are shown in Figures 7 and 8.

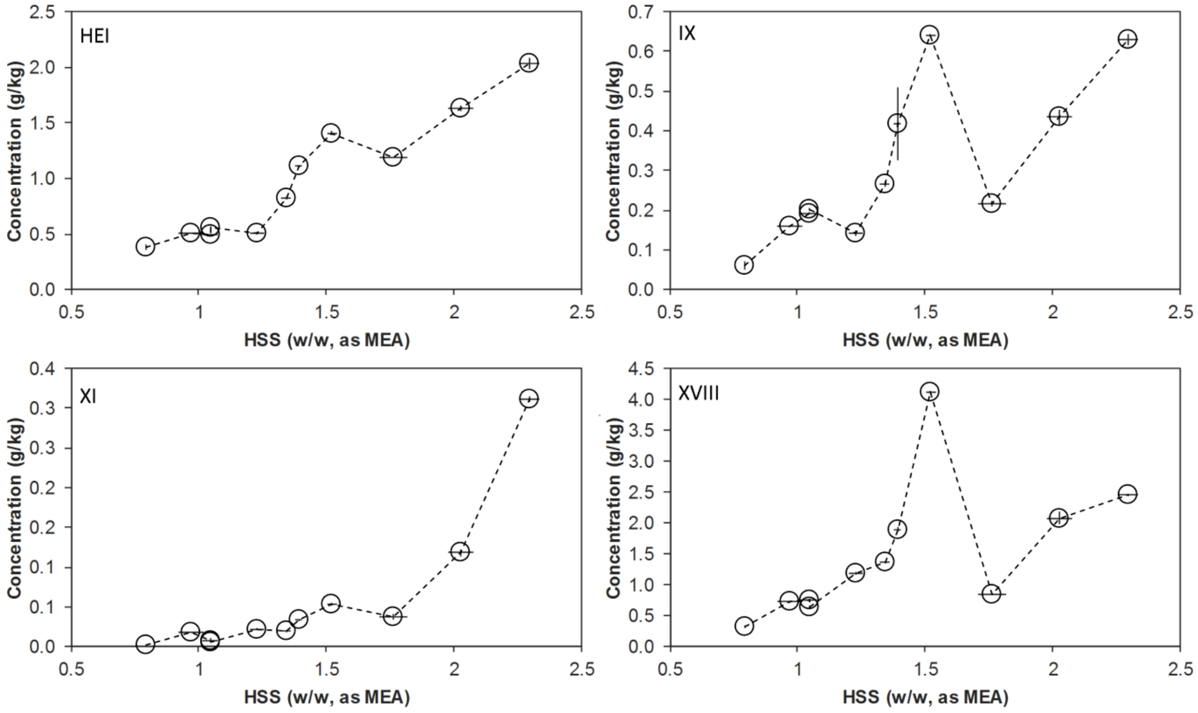


Figure 7. Concentrations of HEI, **IX**, **XI** and **XVIII** in 30% (w/w) aqueous MEA absorbent during pilot scale PCC at Loy Yang

The concentration trends of all the organic degradation products, as shown in Figures 7 and 8, change after the ninth sample. The trends in the ratios of iron, chromium and manganese in the last two or three samples were also distinctly different from the earlier samples from this same sampling campaign. This suggests a change in amine degradation processes between these samples could possibly be a result of changing operating conditions or the composition of the aqueous amine absorbent.

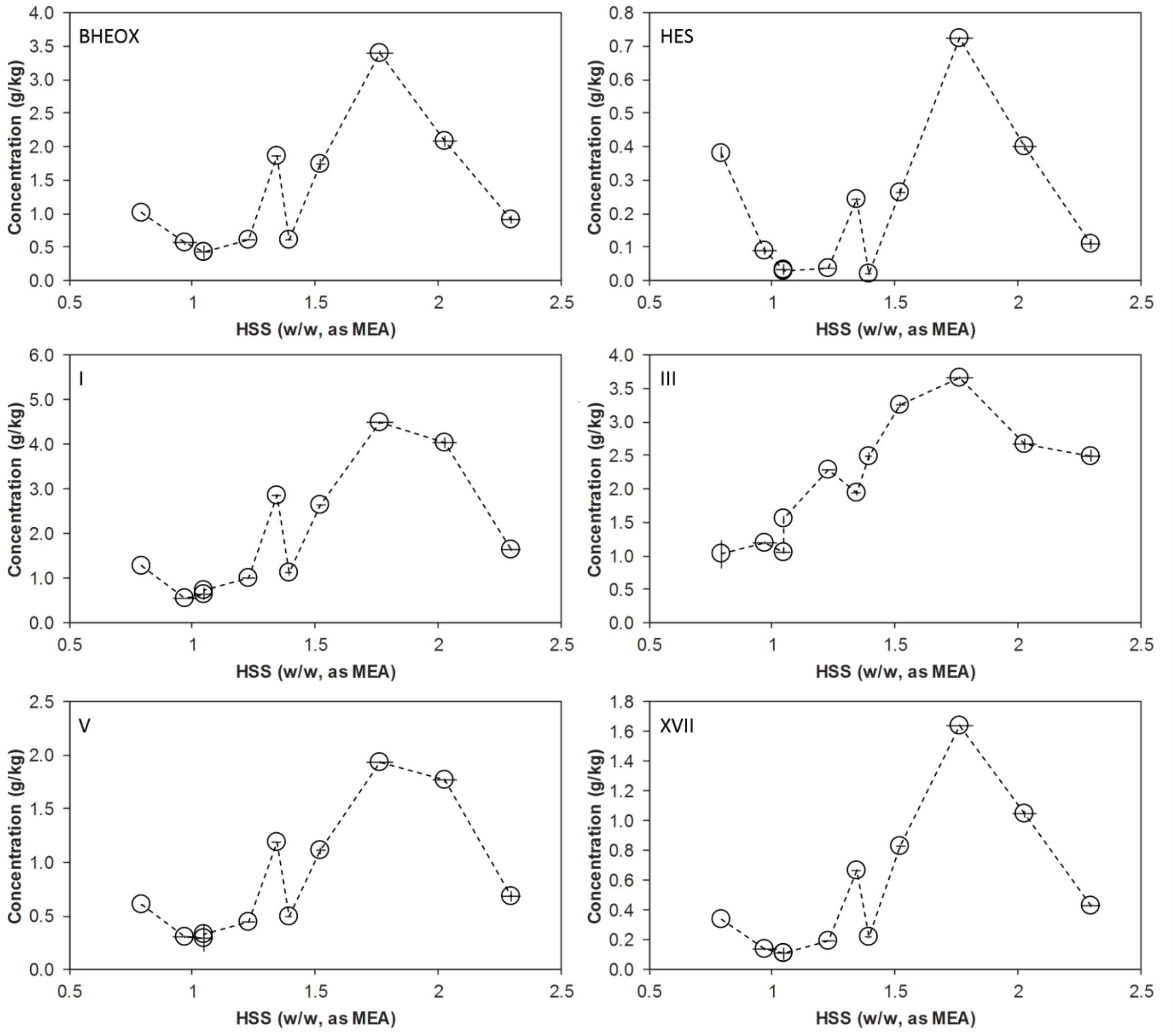


Figure 8. Concentrations of amides (BHEOX, HES, **I**, **III**, **V** and **XVII**) in 30% (w/w) aqueous MEA absorbent during pilot scale PCC at Loy Yang

3.4 Principal component analysis (PCA)

The four principal components identified by PCA accounted for 94% of the variance in the concentrations of the GC-MS target compounds, GC-MS tentatively identified compounds and the organic acids measured by ion chromatography. One of these components correlated strongly with HSS (*r*>0.93) and contained the organic acids as well as HEI. Most of the remaining organic degradation products measured by GC-MS separated into two components depending on which cation exchange fraction they were present in (i.e. *acids and neutrals* or *bases*). The fourth component accounted for the concentrations of the carbamate polymerization product, N-(2-hydroxyethyl)imidazolidione (HEIA). Each of these four components are discussed separately in the following sections.

3.4.1 Heat-stable salts and oxidative degradation products

The PCA vector that accounted for most of the variation in the concentrations of organic acids quantified by ion chromatography, HEI, **XI** and **IX** correlated strongly with HSS (*r*>0.93). These compounds also showed the strongest monotonic increases during this pilot PCC campaign, as shown in Figure 7. HEI has previously been identified as an organic degradation product in both laboratory and pilot scale PCC degradation experiments.[6,16,25] The organic acids (formate, acetate and oxalate) are also products of oxidative degradation and were the most significant contributors to HSS during this pilot PCC campaign (chapter 5).[23]

Figure 9 shows the strong linear correlation between HEI concentration and HSS and Table 3 shows that the measured HEI concentrations increased from 0.379±0.002 to 2.03±0.05 g/kg. Formaldehyde (a precursor to formate) has been identified as a possible precursor to HEI and Figure 9 shows a linear relationship between the formate and HEI concentrations. However, a discontinuity in the correlation is evident between the ninth and tenth sampling events. This discontinuity suggests that HEI production is more sensitive to changes in operating conditions or parameters (Figure 7) than formate production (Figure 6) under the same conditions.

HEI can be measured by UV-Vis (chapter 4)[16] and Figure 9 shows the strong correlation between the increase in absorptivity at 313 nm and HEI concentration. These strong correlations between HSS concentrations, HEI concentrations and UV-Vis absorbance are important evidence that: (a) HEI is a suitable molecular marker for oxidative degradation during PCC and (b) UV-Vis is a suitable technique for monitoring the progress of oxidative degradation during PCC.

The similarity between the concentration trends of **XI** and **IX** with the oxidative degradation products HEI and organic acids suggests that **XI** and **IX** are also oxidative degradation products. Interestingly, both **XI** and **IX** were tentatively identified as HEIA analogues and HEIA is associated with carbamate polymerization.[3,4] The indicative concentrations of **IX** and **XI** remained below 1 g/kg and a distinct change in the trends of the concentrations of each compound was also observed between the ninth and tenth sampling events (Figure 7). Both **IX** and **XI** eluted in the *bases* fraction and have been tentatively identified as cyclic structures with two hydroxyethyl or aminoethyl substituents. Figure 10 shows that **IX** concentration increased linearly with HEI concentration, but **XI** concentration increased exponentially with HEI concentration.

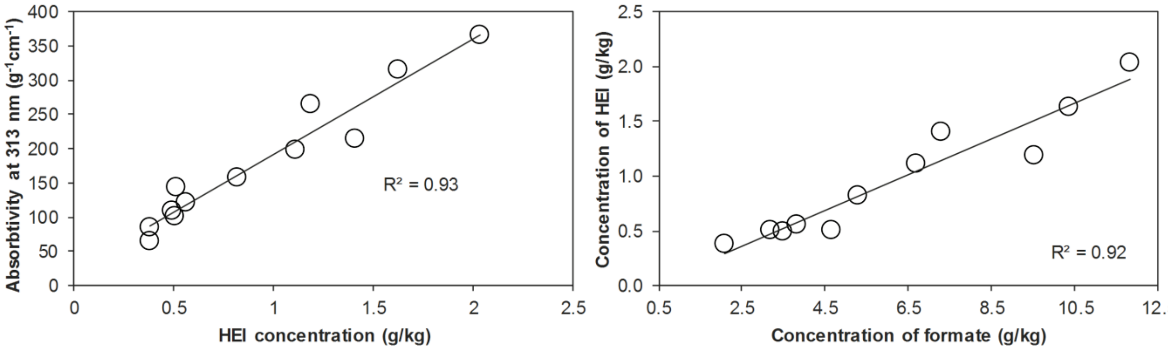


Figure 9. Linear correlations between HEI concentration and the absorptivity at 313 nm and the concentration of formic acid in the 30% (w/w) aqueous MEA absorbent during pilot scale PCC at Loy Yang

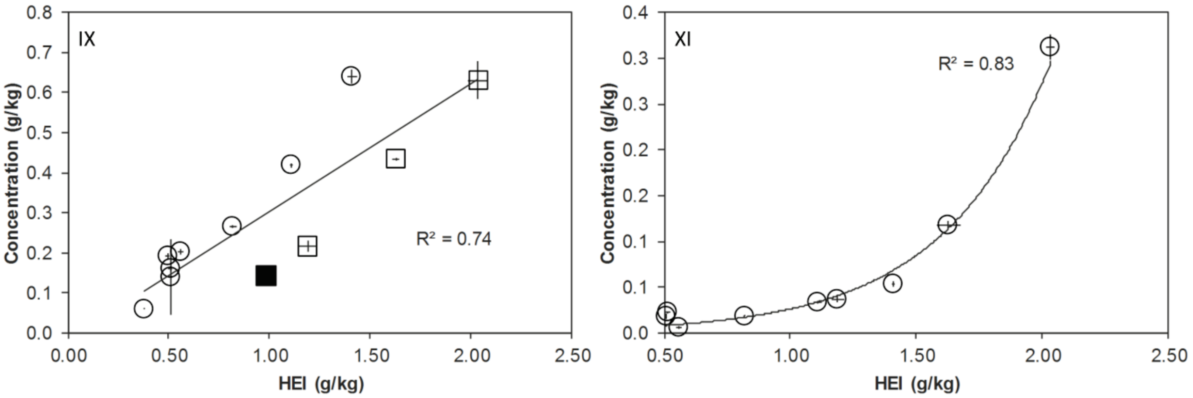


Figure 10. Correlations between the concentration of two tentatively identified compounds present in the bases fraction (**IX** and **XI**) and HEI in the 30% (w/w) aqueous MEA absorbent during pilot scale PCC at Loy Yang. The open square datapoints in the left graph represent the last three samples and the closed square datapoint represents the sample taken from the IBC prior to the PCC campaign at Loy Yang.

Figure 10 shows two separate linear correlations between the HEI and the **IX** concentrations and suggests that there is some difference between these two sets of samples. The three open square datapoints represent the last three sampling events, which have consistently different trends compared to the previous samples. Interestingly, the solid square datapoint represents the sample obtained from the IBC prior to the absorbent being transferred into the PCC pilot plant at Loy Yang. One difference between the pilot plant operating conditions prior to sampling the two types of samples was the number of days that the absorbent had been stored (i.e. not used for PCC): prior to each circular datapoint, the PCC pilot plant had been idle on less than five days (or 25-38% of days); and prior to each open square datapoint, the pilot plant had been idle for more than 13 days (or 46-77% of days).

The distinct separation between these two types of samples suggests that physicochemical characteristics of the MEA absorbent were dependent on the recent operation history of the pilot plant. This observed difference could either result in: (i) ratios of HEI:**IX** concentrations or (ii) different matrix-induced response enhancement effects for these two compounds (chapter 6).[21] However, the linear relationships between UV-Vis absorbance, HEI, HSS and formate concentrations discussed previously, suggest that the changes in HEI concentrations measured in these samples were reliable. Regardless of the reason for the apparent relationship between the ratios of HEI and **IX** concentration, this is an important indication that the operational history of the pilot plant impacted on the physicochemical characteristics of the MEA absorbent. One possible explanation is that MEA degradation was limited by kinetics or oxygen mass transfer during PCC, and these processes were not able to come to equilibrium with the atmosphere without an extended period of absorbent storage.

The exponential correlation between **XI** and HEI concentrations in these samples (Figure 10) also warrants further consideration. One possible explanation for this exponential correlation is that **XI** production was limited by second-order reaction kinetics relative to HEI concentration. As discussed in this section, HEI is an oxidative degradation product and the measured HEI concentrations were linearly correlated with HSS and formate concentrations in these samples. For this reason, the exponential correlation between **XI** and HEI could indicate that **XI** production is limited by second-order kinetics relative to a product of oxidative degradation (e.g. an aldehyde or HSS). This is an important indication that during this PCC campaign, amine degradation was limited by kinetics and/or oxygen mass transfer as suggested by Goff et al.[26]

3.4.2 N-(2-hydroxyethyl)imidazolidione

One PCA component correlated strongly with N-(2-hydroxyethyl)imidazolidione (HEIA). HEIA has been identified as a carbamate polymerization product. Interestingly, no tentatively identified organic degradation products correlated strongly with this component, despite the tentative identification of other imidazolidione analogues in Tables 4 and 5.

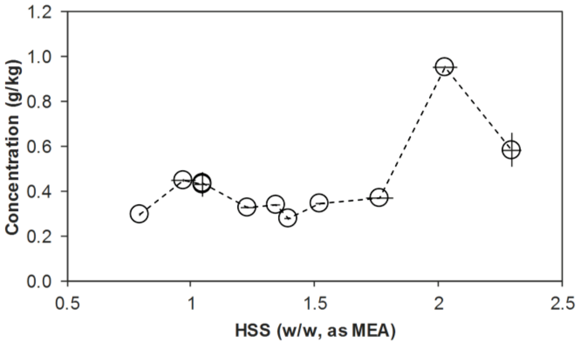


Figure 11. Concentrations of HEIA in 30% (w/w) aqueous MEA absorbent during pilot scale PCC at Loy Yang

During the first part of this pilot PCC campaign, the HEIA concentration remained between 0.28±0.02 g/kg and 0.329±0.005 g/kg and with no significant correlation or monotonic trend with pilot plant operation time or HSS concentration (Table 3 and Figure 11). Interestingly, the HEIA concentrations of the last two samples were significantly higher, 0.95±0.03 g/kg and 0.586±0.007 g/kg, respectively. This is consistent with the differences in the last two or three samples discussed in section 3.4.1 and Figure 11 indicates that the change in conditions also altered the rates of carbamate polymerization reactions.

3.4.3 Acidic and neutral organic degradation products

The organic degradation products that eluted in the acids and neutrals fractions all correlated most strongly with a unique PCA component. N-(2-hydroxyethyl)succinimide (HES) and N,N'-bis-(2-hydroxyethyl)oxamide (BHEOX) accounted for more than 80% of the compounds in this group on a mass basis. These compounds have been previously identified in laboratory scale MEA degradation experiments, although a mechanism for the formation of HES has not yet been formulated.[3] Figure 8 shows that the concentrations of both HES and BHEOX increased prior to the ninth sampling event, before decreasing for the rest of this pilot plant campaign. This suggests that source of HES may be similar to the oxidative degradation origin of BHEOX. The remaining compounds were tentatively identified as amides and were present at less than 5 g/kg, but followed the same trend as the HES and BHEOX.

Unlike these amides, the concentrations of organic acids measured by ion chromatography increased monotonically during this pilot PCC campaign. Changes in the equilibrium between amides and ionized amine and organic anions were also observed during a laboratory scale experiment after the addition of organic acids to a MEA solution.[27] Furthermore, a previous study (chapter 6)[21] suggested that the amide, BHEOX, was converted to an alternative species after addition to these MEA absorbent samples because BHEOX could be recovered accurately from clean 30% (w/w) MEA but was not completely recovered from these degraded MEA absorbent samples. Four possible causes of this change in the equilibrium between amides and ionized MEA and organic anions are: (i) the extended opportunity for the absorbent to come to equilibrium with the atmosphere prior to the last three sampling events discussed in section 3.4.1; (ii) the increase in average ambient temperature during the PCC campaign; (iii) the extended storage time at ambient temperature between pilot plant operation; and (iv) a decrease in alkalinity (or CO_2 capacity) of the absorbent.

MEA is a weak base, and for this reason, as the concentrations of acidic compounds, such as heat-stable salts increase, the equilibrium between MEA and $MEAH^+$ shifts towards $MEAH^+$. This increases the concentration of proton donors (i.e. $MEAH^+$) and could result in the hydrolysis of amides and the concomitant production of amine cations and organic acid anions. The decrease in alkalinity and hydrolysis of amides could lead to an increase in the electrical conductivity, solubility of transition metals and corrosivity. This could be the cause of the change in metal concentrations previously observed during this pilot PCC campaign (chapter 5).[23] Importantly, these results suggest that a decrease in the alkalinity of the lean absorbent could be a critical parameter for managing corrosion, as well as an indicator of severe oxidative amine degradation.

3.4.4 Alkaline organic degradation products

Most of the organic degradation products that eluted in the *bases* fraction correlated strongly with a single PCA component. These compounds were all present at less than 5 g/kg. Figure 8 shows the change in the concentration of **XII** during this pilot PCC campaign and **VI** and **XIV** followed similar concentration trends. The change in concentration of **XVIII** during this pilot PCC campaign is also shown in Figure 7, but unlike the other compounds, **XVIII** increased in concentration between the final three sampling events.

The timing of the disturbance observed in the concentrations of these alkaline organic degradation products is consistent with the change in concentration trend previously in sections 3.4.2 and 3.4.3. However, unlike the acidic and neutral degradation products, the concentrations of these compounds decreased abruptly between the ninth and tenth sampling events. The concentrations of some compounds then remained consistent or increased slightly until the end of the pilot PCC campaign. These observations confirm the presence of a change in the degradation conditions of the MEA absorbent and, as previously observed, this is consistent with the change in dissolved transition metal concentrations.

3.5 Undetected compounds during PCC campaign

A few of compounds that were not detected or identified during this PCC campaign also warrant comment. Firstly, the cation exchange, derivatisation and GC-MS method used in this study was suitable for the quantification of HEEDA (chapter 6)[21] and a reference compound is included in Table 3. However, HEEDA remained below the detection limit throughout this PCC campaign. Although HEEDA is often detected during laboratory scale MEA degradation experiments,[3] it is not always detected in MEA absorbents samples from pilot scale PCC systems.[6,13] Furthermore, very few compounds were tentatively identified as polyamines in Table 5. Two possible exceptions are **XVIII** and **XV**.

The second notable absence is high molecular weight compounds. None of the reference compounds detected in these samples exceeded 200 amu and the largest tentatively identified compounds in Tables 4 and 5 are smaller than 200 amu. The possible exception is **XVIII**, which eluted at 21.1 min and was a broad (or possibly two coeluting broad peaks) on the baseline bleed. In contrast, the use of HPLC with high resolution mass spectrometry enable the identification of compounds with molecular masses up to 273 amu.[28] The indicative concentrations of these compounds ranged from 40 mg/L to 1200 mg/L, which is comparable to the useful concentration range of the cation exchange, derivatisation and GC-MS method used in this study (chapter 6).[21]

3.6. Implications for corrosion and PCC operation

The trends of almost all the organic degradation product concentrations measured during this PCC pilot campaign contain discontinuities prior to the last three sampling events. The only exceptions were the organic acids (acetate, formate and oxalate). Interestingly, these discontinuities in organic degradation product concentrations and the apparent change in corrosion mechanisms and the rapid increase in iron concentrations measured in these same absorbent samples occurred prior to the ninth or tenth sample.[23] This suggests that the increase in iron concentrations and possible change in corrosion mechanism may be associated with these changes in the MEA degradation processes.

The concentrations of the degradation products in each cation exchange fraction were disturbed after the ninth sample, but the concentration profiles differed (Figures 7 and 8). The concentrations of amides and other degradation products in the *acids and neutrals* fraction peaked at the tenth sample and then decreased for the remaining two samples, while the concentrations of alkaline organic degradation products decreased abruptly after the ninth sample. This highlights the reversibility many of the MEA degradation products and indicates that these two classes of compounds responded differently to the change in absorbent conditions. Two possible explanations for this change in degradation processes and associated corrosion are suggested: (i) a decrease in alkalinity; and/or (ii) the impact of the extended opportunity for the absorbent to reach equilibrium with the atmosphere prior to the last three sampling events.

The reduction in alkalinity (i.e. buffering capacity of the CO_2 absorbent) is likely to: (a) increase the concentration of protonated MEA; (b) promote hydrolysis of amides; and (c) increase the solubility of transition metals by increasing the concentration of co-ordination complex ligands such as organic anions and MEA. These changes would result in increased conductivity and corrosivity, as well as reducing the production of carbamate polymerization products because these reaction pathways require condensation of amides. Importantly, this suggests that the alkalinity (or CO_2 absorption capacity) and conductivity of the lean absorbent may be important parameters for monitoring corrosion and amine degradation.

Many of the carbamate polymerization mechanisms that have been proposed include the condensation of an organic acid and an amide.[3] If equilibrium shifted away from amides and towards free organic acid anions and $MEAH^+$ cations following the ninth sampling event, this would also lead to a reduction in the concentrations of these carbamate polymerization intermediates. Many of the proposed carbamate polymerization degradation pathways are expected to be reversible[3] and, for this reason, a decrease in the concentrations of intermediates could also result in a decrease in the concentrations of final products. For these reasons, a decrease in alkalinity could lead to the rapid decrease in concentration and the change in equilibrium observed following the ninth sampling event.

The alternative explanation (the extended opportunity for the absorbent to reach equilibrium with the atmosphere prior to the last three sampling events) could have similar implications. If the limiting factor during this PCC campaign was oxygen mass transfer or kinetics, this would imply that while the PCC plant was operating, oxidative degradation intermediates (including aldehydes) and partially oxidised SO_2 species (including sulfite) would be present in the absorbent. Both aldehydes and sulfite are often used as antioxidants and oxygen scavengers and both have been shown to effectively inhibit MEA oxidation.[9] If the extended opportunities for the adsorbent to come to equilibrium with the atmosphere prior to the last three sampling events enabled the MEA oxidation reactions to proceed to completion, this would imply that all the aldehydes were oxidized to organic acids and/or amides during this time. When the pilot plant operation resumed, aldehydes may no longer be present to preferentially react with oxygen. This reduction in antioxidant capacity could be the cause of the rapid increase in the iron concentration measured in these absorbents. Furthermore, unlike aldehydes, free organic acids are able to conduct electricity and consume alkalinity (i.e. organic acids are heat-stable salts). In addition to lending further weight to the suggestion that conductivity may be a critical parameter for managing corrosion, this alternative explanation may provide an explanation for the apparent reduction in alkalinity and increase in amide hydrolysis.

One important implication of this alternative explanation for the discontinuities in amine degradation observed prior to the last three sampling events is corrosion and corrosion inhibition. If oxidative degradation is controlled by oxygen mass transfer or kinetics under industrial conditions, as dissolved oxygen diffuses into the liquid absorbent, it will be rapidly consumed by partially oxidized species, such as aldehydes and sulfur oxides. In this situation, partially oxidized species could behave as oxygen scavengers or antioxidants and, thus, minimise the need for additional additives and corrosion prevention. However, when the partially oxidized absorbent is stored and oxidation is allowed to proceed to completion or equilibrium with the atmosphere, the antioxidative properties of the absorbent will be consumed. This could lead to higher oxygen concentrations in the absorbent and corrosion. These observations are consistent with previous assessments of the effectiveness of formaldehyde and sulfite for inhibition of metal catalysed MEA oxidation using formaldehyde and sulfite under laboratory conditions.[9,10]

A previous study showed that the iron concentration in the MEA absorbent samples increased linearly with HSS concentration prior to the last two samples and that the main source of iron was corrosion (chapter 5).[23] This suggests that the change in corrosion rate may have been preceded by the change in degradation processes, which lends support to the suggestion that storing the absorbent reduced the oxygen scavenging capacity of the absorbent. If this is true, storage of absorbents and intermittent operation of PCC systems will require careful management to minimize corrosion during use of fresh absorbents and absorbents that have been stored for an extended period of time. However, further experiments at both the laboratory and pilot scales are required to confirm or refute these observations.

4. CONCLUSIONS AND FURTHER WORK

This comprehensive investigation of the degradation of a MEA absorbent during a six month pilot scale PCC campaign provided new and novel insights into MEA degradation, as well as confirming previous laboratory and pilot scale studies. Important observations include: (a) the organic degradation products identified during laboratory scale trials are also produced during pilot scale PCC; (b) the PCC conditions impact on the production of different oxidative degradation products; (c) the production of organic degradation products is related to the concentration of soluble and suspended transition metals; and (d) HEI is a suitable molecular marker for oxidative degradation of MEA. This investigation has also highlighted areas that require further research including: (a) determining the mechanisms of oxidative degradation both in the presence and absence of dissolved transition metals; (b) determining the parameters that limit oxidative degradation during pilot scale PCC; (c) investigating the antioxidative or oxygen scavenging properties of partially oxidised amine absorbents during PCC; and (d) measuring the concentrations of glycine, glycolic acid and other potential organic acids during PCC.

The production of glycolic acid and other organic acids was observed during this pilot scale PCC campaign, but further work is required to: (a) identify organic acids other than acetate, formate and oxalate; and (b) formulate possible reaction mechanisms. The presence of HES was confirmed by GC-MS analysis of a pure standard, suggesting that succinic acid was also produced. N-(hydroxyethyl)glycine was tentatively identified by GC-MS and the production of glycine could be confirmed by the use of a more volatile derivatisation reagent (e.g. trifluoroacetic anhydride) prior to GC-MS analysis.

The strong correlations found between HEI, HSS and formate concentrations are consistent with the identification of HEI as an oxidative degradation product. This correlation confirms that HEI is a suitable molecular marker for oxidative degradation. The use of UV-Vis to monitor HEI production, and, thereby, identify oxidative degradation, was also supported by the strong correlations between HEI concentrations and the absorptivity of the 30% (w/w) aqueous MEA absorbent at 313 nm, which is a characteristic wavelength for HEI. The production of aromatic oxidative degradation products by other aqueous amines indicates that UV-Vis absorbance may be suitable for monitoring oxidative degradation of other amines as well.

The discontinuity between concentrations of degradation products prior to the third sampling event was also of interest. This discontinuity preceded a rapid increase in iron concentrations previously measured in these absorbent samples, leading to the suggestion that the partially oxidized amine absorbent was inherently scavenging oxygen and effectively limited corrosion. However, an alternative explanation for this change in degradation product ratios is a reduction in alkalinity resulting from an increase in HSS concentrations. These two possible explanations have important implications for the operation of PCC systems and for this reason, further laboratory scale experimentation and modelling is required to confirm or refute these suggestions.

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ABBREVIATIONS

BHEOX, N,N'-bis(2-hydroxethyl)oxamide; DEA, diethanolamine; GC-MS, gas chromatography with mass spectrometry detection; HEA, N-(2-hydroxyethyl)acetamide; HEEDA, 2-(2-hydroxyethylamino)ethanol; HEI, N-(2-hydroxyethyl)imidazole; HEIA, N-(2-hydroxyethyl)-2-imidazolidione; HES, N-(2-hydroxyethyl)succinimide; HSS, heat-stable salts; MEA, monoethanolamine; PCC, post-combustion capture of CO_2; SPE, solid phase extraction; SCX, strong cation exchange; UV-Vis, ultraviolet and visible light spectroscopy.

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Chapter 8: Conclusions and future directions

8.1 General discussion

This thesis has presented a comprehensive analysis of MEA degradation and accumulation of impurities during a six month pilot scale PCC campaign at CSIRO's PCC pilot plant at Loy Yang. The methods, data set and findings presented in this thesis will be useful for future research into amine degradation at laboratory, pilot, demonstration and industrial scales. The analytical methods described in chapters 3 and 6 will aid the measurement of and, thereby, investigations into amine degradation during PCC at other installations. The comprehensive data set presented in chapters 3, 4 and 7 of this thesis will assist in the design of laboratory scale experiments to investigate the interactions between amines, cations, metals, inorganics and fly ash particles as well as the modelling of PCC processes and the prediction of emissions to atmosphere, land and water. The findings of this thesis highlight the urgent need to establish the parameters that limit oxidative amine degradation and corrosion during PCC. Together, these three aspects (the analytical methods, the novel dataset and the findings) of this thesis address the eight objectives listed in chapter 1. The achievement of each of these objectives ensured that the aims of this research were also met.

The set of twelve MEA absorbent samples obtained during a six month pilot-scale PCC campaign at CSIRO's pilot plant at Loy Yang is central to this thesis. The range of HSS concentrations (0.797±0.03 to 2.29±0.01 % w/w, as MEA), color and the impact of the amine degradation on the operation and efficiency of the PCC process clearly demonstrate that the condition of this MEA absorbent represented by this sample set is relevant to industrial scale PCC. Spectroscopic, elemental and chromatographic techniques were used to explore the changes in concentrations of organic compounds, metals, inorganic anions and cations in the sample set. This information has provided valuable insights into the amine degradation chemistry and the accumulation of impurities during this pilot scale PCC campaign.

The need to ensure the MEA concentrations measured in these absorbent samples were not adversely impacted by the presence of HSS and other impurities resulted in the development and validation of a GC-FID method. To our knowledge, the GC-FID method described in chapter 3 is the first validation of a GC method for measuring aqueous amine concentrations in PCC absorbents published since 1994. An important advantage of this GC-FID method is the ability to quantify amines other than MEA, including individual species in blended amine absorbents, by simply altering the column oven temperature program. Furthermore, the MEA concentrations measured in these absorbent samples by GC-FID were statistically equivalent to those obtained with the industry standard method, acid-base titration. The development of this GC-FID method also provided valuable insights into the behaviour of aqueous alkaline samples during injection into GC systems and these insights assisted in the development of the more advanced GC-MS method described in chapter 5.

Established spectroscopic and elemental techniques were used to characterise the changes in the composition of the MEA absorbent during the pilot PCC campaign at Loy Yang, as well as to provide insights into suitable methods for on- or at-line monitoring of MEA degradation. A key advantage of many spectroscopic techniques is the ability to measure changes in the organic structure and/or physicochemical environment without disturbing the sample. For this reason, NMR, UV-Vis and ATR-IR spectroscopy were used to complement the cation exchange, derivatisation and GC-MS analyses described in chapter 6 and 7. The agreement between data generated by spectroscopic techniques and the molecular characterisation presented in chapter 7 provide independent confirmation of the accumulation of organic compounds. In particular, both NMR and UV-Vis agreed with the increasing concentrations of N-(2-hydroxyethyl)imidazole (HEI) measured by GC-MS; changes in the ATR-IR spectra agreed with the increasing concentrations of free acids and protonated MEA implied by the decreasing amide concentrations after the ninth sampling event as measured by GC-MS; and the more rapid increase in the concentrations of organic degradation products measured by TOC agrees with the measurement of a large number of neutral or positively ionisable organic compounds in chapter 6. The use of multiple techniques to confirm the strong correlation between amine degradation and the production of HEI provides important support for the use of HEI as a molecular marker for oxidative MEA degradation.

The ability of spectroscopic techniques to measure changes in the organic structure and/or physiochemical environment of these MEA absorbent samples with minimal sample preparation also means that many of these techniques can be adapted for at- or on-line monitoring of amine degradation. Chapter 3 identifies several possible at- or on-line monitoring approaches including: (a) the use of absorbtivity at 270 nm, 278 nm, 305 nm or 313 nm to monitor production of HEI; (b) the use of both MEA and TOC (total organic carbon) concentrations to calculate the concentration of organic degradation products; (c) the measurement of the change in the ATR-IR absorbance at 1602 cm^{-1}, 1629 cm^{-1} or 1639 cm^{-1} for measuring the production of HSS; and (d) the measurement of the intensity of proton resonance either side of the MEA α-amino and/or α-hydroxy resonance. All of these parameters correlated strongly with HSS concentrations, providing confirmation that HSS is a suitable method for assessing the condition of MEA absorbents during PCC.

The UV-Vis absorbance is related to the concentration of HEI (an oxidative degradation product and a molecular marker for oxidative MEA degradation) and the broad absorbance bands of this heteroaromatic compound suggest that the use of simple, robust filter photometers may be suitable for on-line monitoring of HEI production. The IR absorbance bands at 1602 cm^{-1} and 1629 cm^{-1} have been associated with MEA protonation (Richner and Puxty, 2012) and for this reason, the increasing absorbance at these wavelengths is likely to be a result of increasing HSS concentrations. One advantage of the use of ATR-IR absorbance is the potential to use a single technique for the measurement of amine concentrations, CO_2 loadings and amine degradation. The ^1H NMR spectra of these samples of aqueous MEA contained increasing complexity and intensity immediately upfield and downfield of the α-hydroxyl and α-amino MEA resonances. These resonances were assigned to MEA degradation products (including amides and other HSS) and the ratios between the resonances from MEA and MEA degradation products correlated strongly with HSS concentrations.

The accumulation of inorganic anions, cations and metals during the PCC pilot campaign at Loy Yang were measured using ion chromatography and ICP-OES (inductively coupled plasma with optical emission spectrometry detection). The rapid increase in iron concentrations was associated with corrosion and demonstrates that the accumulation of metals is a serious concern for PCC. A change in the ratios of iron, chromium, manganese and nickel after the ninth sampling event suggests that the corrosion mechanisms may have changed during the late stages of this pilot scale PCC campaign. This highlights the urgent need for research into the interactions between amine degradation and corrosion as well as the need to consider alternative materials for PCC systems and column packing.

The high concentrations of transition metals (particularly iron, which increased to 199.0±0.1 mg/kg) measured in these MEA absorbent samples also indicates that an investigation into the partitioning of these metals between co-ordination complexes, hydrated metal ions, metals adsorbed onto surfaces (e.g. ultrafine fly ash particles) and metals present as other non-settable solids is warranted. The partitioning of metals into each of these phases may be important for determining: (a) the mechanisms and rates of catalytic oxidative amine degradation; and (b) the efficiency of simple amine reclamation technologies such as filtering.

Chapter 5 also shows that the accumulation of cations in the MEA absorbent could not be explained by the addition of make-up water or intrusion of the caustic absorbent used to precondition the flue gas. This indicates that the primary source of cations was fly ash and provides further evidence of the need to investigate the interactions between aqueous amines and the ultrafine fly ash particles that are likely to penetrate into PCC absorbers. The high surface area of highly porous, ultrafine fly ash and the acidic nature of the surfaces of the minerals that are likely to comprise ultrafine fly ash particles indicate that there is significant potential for adverse interactions between aqueous amines and these particles.

Interestingly, the accumulation NO_x and SO_x in these MEA absorbent samples contributed fewer HSS (on an acid equivalent basis) than organic anions. The concentrations of organic anions also increased much more rapidly than inorganic anions (sulfate and nitrate). Furthermore, glycolate, acetate and formate were all detected in these absorbent samples, indicating that any of the proposed oxidative degradation mechanisms could have been active during this pilot PCC campaign. Chapter 6 also identifies that the ratio of acetate/formate produced during a PCC pilot campaign at Niederaussem was greater than one (Moser et al., 2011) but this ratio was less than one during the PCC pilot campaign at Loy Yang. This difference in organic acid ratios suggests that the rates of individual oxidative degradation reactions may be dependent on the design and/or operating parameters of different PCC systems. This highlights the need for further research into the mechanisms of oxidative degradation, including the mechanisms of metal catalysis and influences of PCC operating conditions.

To enable reliable quantification of other organic degradation products in these MEA absorbent samples using GC-MS, two sample cleanup methods were developed: cation exchange and dehydration. The robustness of the cation exchange method suggests that the adaption and use of this method for investigating the degradation of other aqueous amine absorbents during PCC is warranted. Chapter 6 also demonstrates the importance of derivatisation prior to GC-MS analysis of these thermally labile, polar degradation products. Opportunities for improving the sensitivity of this cation exchange, derivatisation and GC-MS method were also identified, indicating that versions of this method are likely to be suitable for the analysis of semi-volatile organic compounds in dilute aqueous samples including waste-streams, absorber water wash circuits and for the analysis of atmospheric emissions sampled using suitable impinger media or adsorbents. For these reasons, variations of this GC-MS method are likely to be of significant use for developing a better understanding of amine degradation, atmospheric emissions and the characteristics of aqueous waste produced during PCC.

This cation exchange, derivatisation and GC-MS method was used for the analysis of these MEA absorbent samples. In addition to eight reference standards that had previously been identified as

MEA degradation products, eighteen compounds were tentatively identified from their cation exchange fractionation, GC retention and mass spectral characteristics. Both oxidative degradation and carbamate polymerisation products were identified, providing important validation of previous laboratory scale degradation experiments.

Principal component analysis separated the concentration profiles of these organic degradation products into four groups which were identified as: HSS and oxidative degradation products; amides and other compounds that eluted in the *acids and neutrals fraction*; the carbamate polymerisation product, HEIA [N-(2-hydroxyethyl)-2-imidazolidione]; and other compounds that eluted in the *bases fraction*. Interestingly, chapter 7 shows that the concentration profiles of all organic degradation products other than organic acids contained a discontinuity or disturbance after the ninth sampling event. This discontinuity or disturbance coincided with the change in iron, chromium, nickel and manganese concentration ratios (following the ninth sampling event) and the rapid increase in iron concentrations (following the tenth sampling event).

A comparison of the concentration profiles of the organic acids with the concentration profiles of amides indicate that the portion of organic acids present as amides peaked at the tenth sampling event before rapidly decreasing. This change could be related to a decrease in alkalinity (i.e. due to the accumulation of HSS and/or increases in the CO_2 loading) and could result in increases in: (a) the conductivity of the MEA absorbent; and (b) the availability of co-ordination complex ligands. These changes could lead to a concomitant increases in metal solubility and corrosivity.

In contrast, correlations between the concentrations of HEI and two other tentatively identified organic compounds (**IX** and **XI**) that eluted in the *bases fraction* suggested that some amine degradation processes may be limited by kinetics or mass transfer rather than equilibrium. The exponential relationship of the tentatively identified compound, **XI**, and HEI provided a preliminary evidence of a kinetic or mass transfer limited amine degradation reaction. However, the relationship between HEI and **IX** concentrations exhibited two linear correlations: one for the all MEA absorbent samples up to and including the ninth sampling event; and a different linear correlation for the final three MEA samples. Interestingly, a sample of MEA absorbent obtained from the IBC (intermediate bulk container) prior to the pilot scale PCC campaign at Loy Yang was consistent with the linear correlation between HEI and **IX** for the final three MEA samples from the pilot plant. A key similarity between these last three MEA absorbent samples and the MEA absorbent obtained from the IBC could be the extended period of storage prior to each sampling event. For this reason, it is suggested that a possible explanation for these concentration profile discontinuities is kinetic or mass transfer (e.g. oxygen mass transfer) limits on MEA degradation reactions.

Previous laboratory based experiments have suggested that oxidative degradation of MEA in the presence of metals is likely to be limited by oxygen mass transfer during industrial PCC (Goff and Rochelle, 2004; Léonard et al., 2014a). If these MEA degradation processes are limited by oxygen transfer, storing the absorbent in contact with the atmosphere for an extended period of time would enable these processes to reach equilibrium and/or proceed to completion. However, during continuous PCC operation, the intermediates of oxidative reactions (including aldehydes from oxidative MEA degradation and sulphites from oxidation of SO_2) are likely to be present in the absorbent. Both sulphites and aldehydes are effective inhibitors of MEA degradation (Goff and Rochelle, 2006) and the rapid increase in iron concentrations following the ninth sample could possibly be a result of the depletion of these oxygen scavengers during extended periods of absorbent storage. The complete oxidation of aldehydes to organic acids and sulfite to sulfate could also be the source of decreasing alkalinity implied by the shift towards hydrolysis of amides. However, further research is needed to confirm or refute these hypotheses.

In general, carbamate polymerisation products such as HEIA and polyamines were present at much lower concentrations than oxidative degradation products and, for this reason carbamate polymerisation is not likely to result in significant consumption of amines. However, the interactions between oxidative degradation, corrosion and carbamate polymerisation are poorly understood and further research in this area is also warranted.

8.2 Conclusions and future directions

The detection and identification of organic acids, HEI, N-(2-hydroxyethyl)-2-imidazolidione (HEIA) and other organic compounds confirmed that both oxidative degradation and carbamate polymerisation reaction pathways were active during this PCC campaign at CSIRO's pilot plant at Loy Yang. Other active reaction pathways included corrosion and oxidation of SO_x. Importantly, the organic compounds produced during this PCC campaign indicate that laboratory scale MEA degradation experiments are representative of the MEA degradation that occurred during this pilot scale PCC campaign.

Oxidative degradation was the main MEA degradation reaction pathway with the most significant influence on the condition of the MEA absorbent sampled from CSIRO's pilot PCC plant at Loy Yang. However, the accumulation of metals, inorganic anions and cations from fly ash were identified as significant concerns for the continuing use of this absorbent for PCC. Further work is needed to characterise and quantify the interactions between oxidative amine degradation, metals and the mineral surfaces of ultrafine fly ash.

Organic acids and heat-stable salt concentrations remain effective indicators of amine damage. However, the production of heteroaromatic compounds by oxidative degradation provides excellent molecular markers for amine degradation. The most concentrated heteroaromatic produced during the use of this MEA absorbent at CSIRO's PCC pilot plant was HEI [N-(2-hydroxyethyl)imidazole]. The production of this oxidative degradation product is easily measured by UV-Vis absorbance at 313 nm. The UV-Vis absorbance of HEI is broad and easily distinguishable, suggesting that HEI production can be possibly measured using simple, robust filter spectrophotometer instrumentation during PCC.

The research presented in this thesis highlights the importance of managing metal concentrations, corrosion and intrusion of fly ash during PCC from coal-combustion flue gases. One promising method for minimising corrosion is the use of alternative materials for the construction of PCC systems and column packing components. Replacing the large surface area of the metal packing material in the absorber and desorber columns with polymer packing material would significantly reduce the surface area of metal in contact with aqueous amine absorbents. However, determining the mechanisms of metal catalysed oxidative degradation is also likely to assist in the selection and development of other strategies and/or additives for minimising oxidative amine degradation.

An additional consideration for the management of amine condition during PCC identified in this thesis is the oxygen scavenging activity of aldehydes and sulphites. Aldehydes are intermediates of amine oxidation and sulphites are intermediates in the oxidation of SO_2, and for these reasons, both aldehydes and sulphites are produced during PCC from gases containing oxygen and SO_x. Both of these classes of compounds are effective MEA oxidation inhibitors. During this PCC campaign at Loy Yang, changes in the concentrations of transition metals (including iron) and organic degradation product concentration profiles coincided. One possible explanation is that the extended periods of MEA absorbent storage prior to the last three sampling events allowed time for sufficient oxygen mass transfer for complete oxidation of the aldehydes and sulphites, thus removing the inherent antioxidant properties of the MEA absorbent and allowing corrosion to proceed. However, further research is required to confirm or refute these hypotheses.

This thesis also highlights the importance of amine reclamation strategies for: (a) maintaining the CO_2 absorption capacity of the absorbent; and (b) the removal of contaminants that are likely to promote amine degradation. The removal of heat-stable salts remains an important component of amine reclamation to maintain the CO_2 absorption capacity of the absorbent and this requires the hydrolysis of heat-stable salts and the removal of anions. However, the removal of metals and ultrafine fly ash particles from the absorbent will also be important in minimising amine damage during PCC. Further research into the interactions between metals, aqueous amines and the mineral surfaces of ultrafine fly ash particles is needed to: (a) determine whether or not the mineral surfaces of ultrafine fly ash particles are likely to catalyse or promote amine degradation; and (b) determine what technologies are likely to remove these ultrafine particulates from aqueous amines most effectively.

In addition to collating a valuable data set describing the degradation of MEA and the accumulation of inorganic anions, cations and metals in an MEA absorbent used for pilot scale PCC at CSIRO's Loy Yang pilot plant, this thesis has highlighted the urgent need for research into the interactions between aqueous amines, metals and mineral surfaces of ultrafine fly ash particles. In particular, this thesis has identified and/or highlighted the need for further research in the following areas:

1. Oxidative degradation

   The products of oxidative degradation under laboratory conditions are fairly well understood, but further information about the mechanisms is required to enable optimum control of oxidative amine degradation during PCC. Laboratory based investigations are needed to establish: (i) the mechanisms of oxidative degradation in the presence and absence of transition metals; (ii) the potential influences of ultrafine fly ash of oxidative degradation; and (iii) the effects of limited oxygen mass transfer on the products and mechanisms of oxidative degradation. Investigations into the mechanisms of oxidative amine degradation in the presence of sulphite are also warranted.

   Further research into oxidative degradation is also needed at pilot, demonstration and industrial scales. The preliminary evidence for the production of different ratios of organic acids warrants further investigation because this may indicate that oxidative degradation mechanisms are influenced by operating parameters. The preliminary evidence for the production of organic acids other than acetate and formate (e.g. glycolate and succinate) requires further research. Confirming or refuting the production of glycine during PCC using MEA absorbents would also provide important insights into the production of HEGly [N-(2-hydroxyethyl)glycine] and HEPO [N-(2-hydroxyethyl)piperazin-2-one].

2. Corrosion

   Previous studies have demonstrated that corrosion rates of 316 stainless steels are acceptable for ensuring structural integrity. However, corrosion also increases the concentrations of transition metals in the absorbent and this could be problematic for PCC using amine-based absorbents. Hence, there is a need to determine what metal concentrations (and thereby, corrosion rates) can be tolerated in amine absorbents during PCC.

   This thesis also provides preliminary evidence for a change in corrosion mechanisms during this PCC campaign. This highlights the need to determine: (i) the corrosion mechanisms that occur during pilot scale PCC; (ii) the effects of PCC operating parameters on these corrosion mechanisms; and (iii) the effects of amine degradation products and impurities on these corrosion mechanisms.

3. Strategies for inhibiting corrosion and oxidative amine degradation

   One strategy for minimising corrosion during PCC is the use of non-metal materials for column packing and other components that are in contact with amine-based absorbents. This would reduce the concentrations of metals in the absorbent, and therefore, be an effective strategy for limiting metal catalysed oxidative amine degradation. Alternative strategies include the use of anticorrosion and/or antioxidant additives.

   The timing of changes in the concentration profiles of both metals and organic degradation products suggested that intermediates produced during PCC may have inhibited corrosion. The anticorrosive properties of the absorbent may have been aldehydes and sulfites because these compounds are produced during PCC and effective oxygen scavengers. The stability, reactivity and other characteristics of these compounds during PCC require further investigation to provide guidance for balancing the contrasting priorities of: (i) anticorrosive and oxygen scavenging capacity; and (ii) amine degradation. Further research into implications for intermittent PCC operation, storage of amine-based absorbents and the use of fresh absorbents is also warranted.

4. Interactions between amines, transition metals and ultrafine fly ash

   This thesis demonstrated that both transition metals (primarily from corrosion) and cations (associated with fly ash) accumulated in MEA absorbent during the PCC campaign. Transition metals are known to catalyse oxidative degradation, but other interactions between transition metals and amines are also possible; for example, amines often form co-ordination complexes with metals. This thesis provides information about the concentrations of a range of transition metals that are likely to be present in amine absorbents, thereby, providing necessary information for preliminary assessments of the impacts that amine-metal complexes could have on the CO_2 capture efficiency and capacity of amine-based absorbents.

   The accumulation of ultrafine fly ash in amine-based absorbents highlights the importance of research into interactions between aqueous amines and these highly porous, mineral particles. Fly ash is unlikely to be a significant source of transition metals unless non-metallic materials are used for the construction of PCC systems and column packing materials. However, the large surface area of ultrafine fly ash could provide important surfaces for adsorption of transition metals from corrosion and this could enable very high concentrations of metals to accumulate in amine-based absorbents. For these reasons, further research is required to investigate: (i) heterogeneous reactions between aqueous amines, fly ash and metals adsorbed onto mineral surfaces; and (ii) the efficiency of filtration for the removal of both fly ash minerals and adsorbed metal ions.

5. Amine reclamation strategies

   The findings of this thesis highlight the need for amine reclamation technologies and processes that are effective at: (i) reducing metal concentrations; (ii) removing ultrafine fly ash particles; and (iii) removing organic degradation products. This will require the hydrolysis of amides as well as the removal of both anionic and cation species. A wide range of technologies are available for amine reclamation and there is a need to incorporate amine reclamation into pilot scale PCC campaigns.

6. Measurement methods

   As PCC proceeds towards commercial scale, the analytical methods used to identify and quantify organic degradation products in samples from PCC systems (including absorbents, liquid wastes, solid wastes and amine reclaimer process streams) will be need to satisfy the data quality standards of regulatory authorities. However, very few studies report sufficient method development data. There is significant scope to improve, modify and adapt the GC-MS method described in chapter 6 for these purposes and a recent study has explicitly validated a HPLC-MS method. However, there is a clear need to incorporate rigorous analytical method and data validation practices into laboratory and pilot scale PCC studies.

   This thesis has proposed a number of promising methods for monitoring amine degradation during PCC. Further research is needed to demonstrate and integrate these methods into pilot and other industrial PCC systems. Further research is also needed to adapt, modify and validate these methods for alternative amine absorbents, PCC process streams and PCC systems.

Other important outcomes of this thesis include: (a) the identification of HEI as a suitable molecular marker for oxidative degradation of MEA; (b) evidence for different oxidative degradation mechanisms occurring at different rates during PCC at different pilot plants; (c) evidence for a change in corrosion mechanisms during this PCC campaign at CSIRO’s pilot plant at Loy Yang; and (d) the measurement of a change in the portion of oxidative degradation products present as amides versus free acids and $MEAH^+$ species. This thesis also describes GC methods that will improve the ability of researchers to measure and identify organic degradation products of aqueous amines during laboratory, pilot, demonstration and industrial scale PCC experiments and processes.

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Appendix A

A paper presented to the 11th International Conference on Greenhouse Gas Technologies in Kyoto during November 2012 is attached as an appendix. The full reference for this paper is:

Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Meuleman, E., Chaffee, A., Cottrell, A.J., Feron, P., 2013. Chemical characterization of MEA degradation in PCC pilot plants operating in Australia, Energy Procedia, pp. 877-882.

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Chemical Characterization of MEA Degradation in PCC pilot plants operating in Australia

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Abstract

An important step towards commercial scale post-combustion CO_2 capture from coal-fired power stations is understanding solvent degradation. Laboratory scale trials have identified three main solvent degradation pathways for 30% MEA: oxidative degradation, carbamate polymerization and formation of heat stable salts. This paper probes the semi-volatile organic compounds produced from a single batch of 30% MEA which was used to capture CO_2 from a black coal-fired power station (Tarong, Queensland, Australia) for approximately 700 hours, followed by 500 hours at the brown coal-fired power station (Loy Yang, Victoria, Australia). Comparisons are made between the compounds identified in this aged solvent system with MEA degradation reactions described in literature.

Most of semi-volatile compounds tentatively identified by GC/MS have previously been reported in laboratory scale degradation trials. Our preliminary results show low levels of degradation products were present in samples after its use in the pilot plant at Tarong (black coal) and consequent 13 months storage, but much higher concentrations were later found in the same solvent during its at use in the pilot plant at Loy Yang Power (brown coal). Further work includes identifying the cause of poor GC/MS repeatability and investigating the relative rates of reactions described in literature. The impact of inorganic anions and dissolved metals on MEA degradation will also be explored.

Keywords: monoethanolamine; degradation; black coal; brown coal; post-combustion CO_2 capture

1. Introduction

Considerable progress has been made in the development of aqueous amine chemical absorption for post-combustion CO_2 capture (PCC) from coal-fired power stations. One important aspect of current research programs world-wide is understanding the chemical degradation reactions and associated emissions to air, water and other wastes that occur in pilot scale PCC plants [1-7].

The three most rapid MEA degradation reaction pathways (formation of heat stable salts, oxidative degradation and carbamate polymerization) have been studied extensively at the laboratory scale [8-17] and some work has been done at the pilot [5, 18] and commercial scale [19]. Both organic and inorganic compounds are involved in these reactions and a wide range of analytical techniques are required to fully understand the chemical changes in PCC solvents during operation.

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Gas chromatography mass spectrometry (GC/MS) is one technique that has been used to tentatively identify some products of MEA degradation [16, 19]. The primary disadvantage of GC is that compounds must be stable and volatile at approximately 300°C to 500°C (commonly called *semi-volatile* compounds). However, compared to liquid chromatography mass spectrometry (LC/MS), the gaseous eluate from a GC is easily ionized (often using the very reproducible and robust electron impact) and introduced to a high vacuum MS system. Unlike LC/MS, GC/MS usually separates the solvent from the analytes, providing higher quality spectra that can often be identified by comparison with reference spectra from mass spectral libraries. However, unequivocal identification requires the comparison of sample retention time and mass spectra with pure standards.

This paper reports some preliminary findings from the analysis of 30% MEA solvent sampled during operation at coal-fired power station PCC pilot plants at Tarong and Loy Yang Power operated by CSIRO. CSIRO operate PCC pilot plants at both black and brown coal-fired power stations in Australia. One PCC pilot plant is located at Stanwell's 1400 MW black coal-fired power station at Tarong (Queensland) and another is located at Loy Yang Power's 2210 MW brown coal-fired power station at Loy Yang Power (Victoria). Details of these pilot plants are available elsewhere [20]. Recently, a single batch of 30% (w/w) MEA (monoethanolamine) has been used at both of these pilot plants as part of a research program focused on the formation and emission of MEA degradation products.

2. Materials and Methods

In this study, MEA was used to capture CO_2 at a PCC pilot plant operated by CSIRO for approximately 700 hours at Tarong. The solvent was then stored for 18 months in a plastic intermediate bulk container (IBC) before capturing CO_2 at CSIRO's PCC pilot plant at Loy Yang Power for a further 500 hours. The samples are described in Table 1.

Table 1. Description of solvent samples

Sample origin	Date sampled (dd/mm/yyy)	Solvent operating time (h)
Tarong	2/12/2010	8
Tarong	6/01/2011	71
Tarong	11/02/2011	170
Tarong	14/03/2011	250
Tarong	30/03/2011	330
Tarong	13/04/2011	390
Tarong	13/05/2011	510
Loy Yang	2/08/2012	733
Loy Yang	14/08/2012	790
Loy Yang	21/08/2012	840
Loy Yang	29/08/2012	920
Loy Yang	4/09/2012	970
Loy Yang	11/09/2012	1040
Loy Yang	18/09/2012	1100

Solvent samples were taken in acid washed high density polypropylene bottles and transferred immediately to the laboratory in dark containers containing ice bricks. On arrival at the laboratory, samples were diluted within 2 hours, stored at 4ºC and analyzed within a fortnight. The diluted aqueous MEA samples were analysed without prefractionation or derivatisation. Approximately 100 mg of sample was weighed into a tared amber, silanized GC vial and made up to approximately 1.00 g with 0.1% ammonium hydroxide containing 25 mg/L d_5-pyridine. A 5µL syringe was used to inject 0.2 µL into a Varian CP3800 GC with a 30m x 0.25 mmID 1 µm 5% phenyldimethylsiloxane column (Agilent, CP8949) and Varian Saturn 2000 ion trap mass spectrometer. The injector (model 1177) was held at 280ºC with a 1:30 split and helium was used as a carrier gas. The column oven was programmed to heat from 60°C to 80°C at 2°C/min, to 320°C at 12°C/min and hold at 320°C for 3 min. The mass spectrometer was programmed to scan from 29 *m/z* to 200 *m/z* (3 to 15 min) and from 29 *m/z* to 400 *m/z* (15 to 33 min). The ion trap storage level was reduced from the default to 28 m/z and the scan rate was increased to 0.5 s/scan.

Tentative identifications were assigned to compounds based on their retention times, comparison with reference spectra (NIST/EPA/NIH Mass spectral library, version 2.0, 26/04/2012) and compounds reported in literature.

3. Results and Discussion

GC/MS total ion chromatograms in Fig. 1. reveal that few volatile or semi-volatile degradation products were present in the samples taken from the PCC pilot plant at Tarong (chromatograms (a) and (b) in Fig. 1.). The relative abundance of degradation products in samples taken from the first sample of the pilot plant at Loy Yang Power may either have resulted from their accumulation during solvent storage or be due to their presence in the PCC pilot plant at Loy Yang Power prior to introducing the MEA solvent. The samples also contain low levels of other aqueous amine PCC solvents from previous campaigns at Loy Yang Power. Importantly, increases in the concentrations of degradation products are evident during the 370 hours of operation at Loy Yang Power.

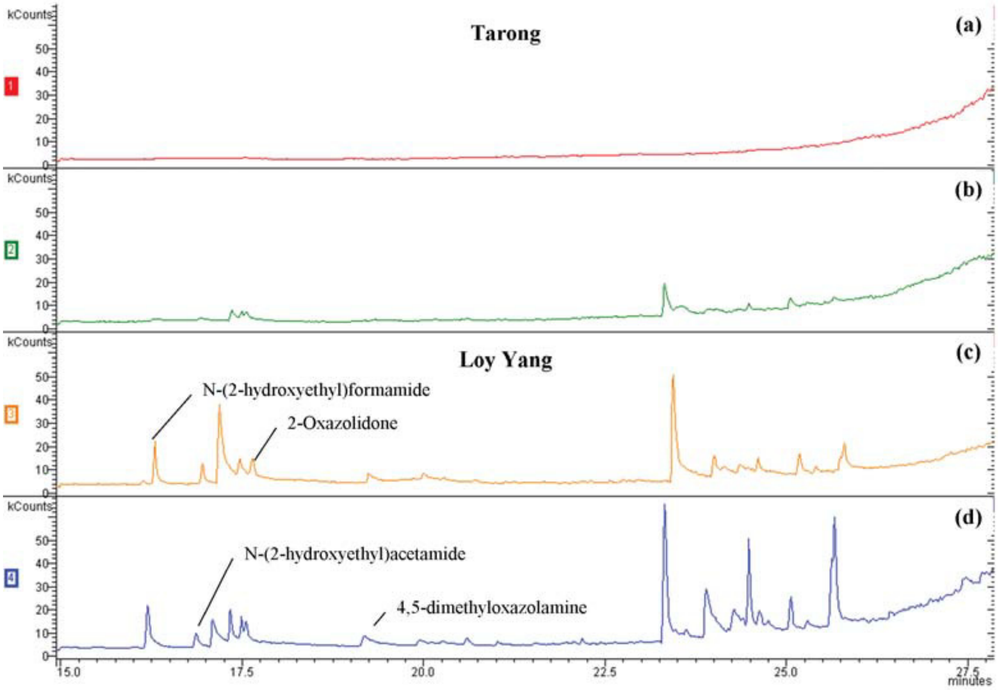

Fig. 1. GC/MS total ion chromatograms of samples taken on the (a) 2/12/2010, (b) 13/05/2011, (c) 2/08/2012 and (d) 18/09/2012 diluted 1:10 in 0.1% ammonium hydroxide. (a) and (b) were sampled from the pilot plant at Tarong. (c) and (d) were sampled from the pilot plant at Loy Yang Power.

Interestingly, the compounds in Fig. 1. are grouped within two distinct molecular weight ranges of MEA degradation products. The first group of compounds have a molecular weight range of 100 to 120 amu and are adducts of at least two MEA or degradation product molecules. The second group of compounds (150 to 200 amu) and are adducts of more than two MEA or degradation product molecules.

Tentative identifications for semi-volatile compounds present in the 30% MEA samples are listed in Table 2. Many of the compounds reported in literature have also been tentatively identified in aged samples of 30%

(w/w) MEA from PCC pilot plants at Tarong and Loy Yang Power. This indicates that degradation reactions of MEA during pilot plant operation were similar to reactions described in literature from both laboratory and field trials.

Table 2. Tentative identification of volatile compounds present in MEA samples from the pilot plants at Tarong and Loy Yang

Retention time (min)	Identification	Present in other references	Mass spectrum
5.12	?Oxazolidine		43 (100); 46 (96); 72 (61)
16.2	MW 127: possibly N-2,3dimethyl-2-butendiamine		32 (100); 97(72); 69 (43); 96 (40)
16.3	N-(1-hydroxyethyl)formamide	[19] [15]	59 (100); 90(79); 46(58); 58(44)
16.9	N-(1-hydroxyethyl)acetamide	[19] [16] [9]	43(100); 60(58); 73(38); 85(19)
17.6	2-oxazolidone	[19] [14]	87(100); 42(42); 87(23); 57(21)
19.2	MW 112: possibly uracil or 4,5-dimethyl-2-oxazolamine	[16]	112(100); 69(90); 81(86); 54(83);72(58)
19.9	N-(2-hydroxyethyl)lactamide	[19]	45(100); 70(99); 90(84); 115(28); 88(34)
20.6	N-(2-hydroxyethyl)succinimide	[19] [16] [9]	100(100); 55(43); 84(38); 113(34); 72(162)
22.1	1-(2-hydroxyethyl)imidazolidinone	[19] [16] [9] [14] [11] [9]	99(100); 56(37); 100(36); 70(23); 42(16)
23.3	1-hydroxyethyl-2-piperazinone	[9] [14] [19]	113(100); 85(97); 56(44)
23.9	Methyldiethanolamine or diisopropanolamine	[9]	88(100); 70(33); 42(18); 44(15)
24.3	2-(2-aminoethyl(amino)-ethanol	[16] [11] [9]	74(100); 56(52); 44(17);
24.5	?MW 157?		157(100); 56(82); 86(32); 74(32); 88(27)
25.1	? possibly MW 171		56(100); 171(45); 172(35)
25.6	? possibly MW 202		171(100); 42(89) 143(66); 86(55); 74(42); 72(35); 202(22)

MW: molecular weight

The increasing variance of replicate analyses with longer solvent operating times as shown in Fig. 2. was also observed for other tentatively identified compounds. This increased variability was observed despite the relatively precise replicate analyses of 2-oxazolidone in samples between 0 and 400 operating hours obtained immediately following the analysis of samples taken after 970 hours of operation. The absence of significant changes in peak shapes also suggests that the variability is related to the age of the sample rather than poor GC/MS performance. Non-volatile heat stable salts and other inorganics (such as corrosion metals) are known to accumulate in aqueous MEA solvents used to capture CO_2 [5, 18, 21]. These compounds are a likely cause of the GC/MS variability observed in this work.

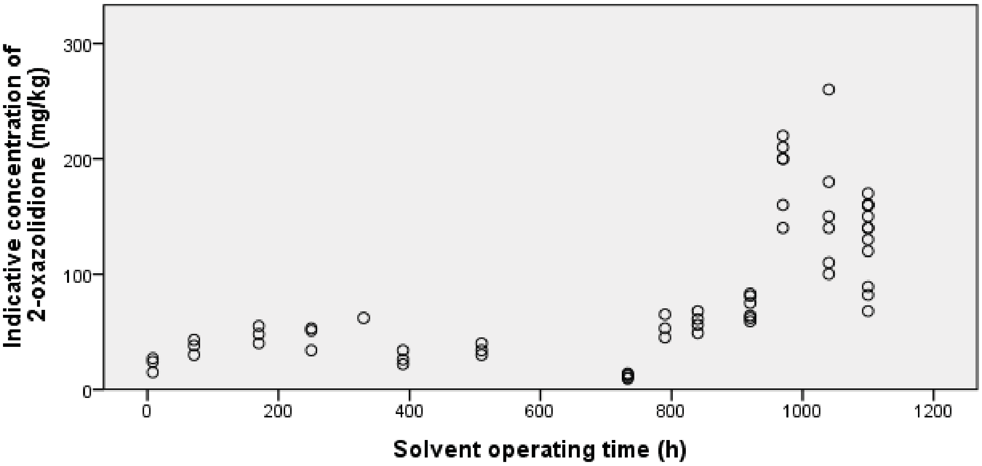

Fig. 2. Indicative concentrations of 2-oxazolidone in solvent samples from the pilot plants at Tarong and Loy Yang Power versus operation time.

4. Conclusions

Overall, this data indicates that MEA degradation products identified during laboratory scale trials are also produced during pilot scale PCC. Once the causes of variability of GC/MS data are resolved, the relative rates of oxidative degradation and carbamate polymerization will be investigated. Further work is also in progress to investigate the accumulation of inorganic anions and metals in MEA solvent systems under pilot plant PCC conditions.

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Appendix B

Sample parameters and concentration of MEA, CO_2 and HSS (Table B1). As received concentrations and quality control data of anions (Table B2), metals (Table B3), cations (Table B4) and target organic compounds (Table B5).

Table B1. Descriptions and concentrations of MEA, CO_2 and HSS of the 30% MEA absorbent samples

Sample ID	Operating hours*	CO_2 captured (t)*	MEA concentration (% w/w)		CO_2 (mol CO_2/kg)		HSS (% w/w, as MEA)	
			m	MD	m	MD	m	MD
D4	5	0.12	35	0.62	1.2	0.013	0.80	0.029
E4	57	1.15	30	0.60	1.4	0.013	0.90	0.028
F4	110	2.41	32	1.6	1.2	0.0067	1.0	0.026
G4	190	3.85	27	0.24	1.0	0.021	1.0	0.019
H4	240	4.91	27	0.67	1.0	0.0049	1.0	0.012
I4	310	6.04	31	0.09	1.1	0.0044	1.2	0.018
J4	370	7.26	29	0.40	1.1	0.0067	1.3	0.056
K4	510	9.81	31	0.78	0.68	0.0007	1.4	0.051
L4	560	10.6	27	0.47	0.66	0.0011	1.5	0.040
M4	680	12.1	28	0.60	0.77	0.0027	1.8	0.010
N4	800	13.7	27	0.84	0.48	0.0024	2.0	0.060
O4	830	14.1	27	1.0	0.59	0.0073	2.3	0.015
Quality control parameters								
MDL			1		0.01**		0.026	
PQL			5		0.05		0.13	
%RPD								
E4							6	
J4			0.4		3			
K4					6			
Recovery (%)								
J4			104		101			
K4					108			
Control standard			97		93*		85	

*, excludes operating time and CO_2 captured at CSIRO's pilot plant at Tarong; **, estimated

Table B2. Concentrations, recoveries and repeatability of anions in the 30% MEA absorbent samples

Sample ID	Acetate (g/kg)		Formate (g/kg)		Chloride (g/kg)		Nitrite (g/kg)		Nitrate (g/kg)		Sulphate (g/kg)		Oxalate (g/kg)	
	m	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**
D4	2.1	0.059	2.1	0.027	0.10	0.00012	ND	ND	0.60	0.020	1.5	0.019	0.52	0.010
E4	2.3	0.031	2.7	0.025	0.12	0.0066	ND	ND	0.71	0.0080	1.7	0.035	0.63	0.021
F4	2.6	0.025	3.2	0.032	0.12	0.0005	0.11	0.0028	0.72	0.010	1.8	0.027	0.78	0.014
G4	3.0	0.020	3.5	0.011	0.13	0.0008	0.11	0.0022	0.78	0.025	1.8	0.016	0.90	0.015
H4	3.0	0.012	3.8	0.016	0.14	0.0020	0.11	0.0012	0.82	0.038	1.8	0.012	1.0	0.016
I4	3.1	0.012	4.7	0.016	0.15	0.0012	0.11	0.0009	0.91	0.035	2.0	0.020	1.1	0.017
J4	3.0	0.015	5.3	0.033	0.15	0.00086	0.11	0.0011	1.1	0.026	2.0	0.015	1.1	0.0058
K4	4.1	0.035	6.7	0.050	0.16	0.0012	0.12	0.0029	1.2	0.013	2.1	0.010	1.5	0.044
L4	3.9	0.013	7.3	0.016	0.16	0.010	0.11	0.0019	1.2	0.018	2.1	0.029	1.5	0.041
M4	3.5	0.13	10	0.19	0.17	0.0043	0.12	0.0057	1.4	0.024	2.4	0.13	1.9	0.11
N4	4.6	0.14	10	0.21	0.16	0.00073	ND	ND	1.5	0.034	2.2	0.0094	2.7	0.059
O4	5.1	0.063	12	0.10	0.17	0.0011	ND	ND	1.5	0.016	2.4	0.072	3.1	0.22
Quality control parameters														
MDL	2.8		0.26		26		22		23		22		93	
PQL	14		1.3		128		108		116		112		465	
%RPD														
E4	21		16		4.5		NA		1.2		2.4		3.3	
N4	5		5		0.1		NA		3.0		2.0		3.5	
Recovery (%)														
30% MEA	NR		89		85		NA		87		96		NA	
E4	44^		100		75		89		89		89		105	
N4	54^		96		77		89		86		91		NA	
Control standard*	NA		NA		96		NA		87		96		NA	

*, control standard was from ERA, Golden, CO (catalogue number 981, Ion Chromatography); ^, Acetate was spiked at less than 2 times the PQL; m, mean of triplicate measurements; MD, mean deviation of triplicate measurements; MDL, method detection limit; NA, not applicable; NR, measured concentration was less than the PQL; PQL, practical quantitation limit; RPD, relative percent difference

Table B3. Concentrations, recoveries and repeatability of metals and cations in the 30% MEA absorbent samples

ID	**Ca**		**Cr**		**Cu**		**Fe**		**K**		**Mg**		**Mn**		**Mo**		**Na**		**Ni**		**V**		**Zn**	
	m	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**
D4	9.8	0.14	1.2	0.017	2.7	0.039	14	0.27	6.3	0.12	2.4	0.038	0.48	0.0067	0.21	0.00029	18	0.33	2.2	0.043	0.32	0.0019	5.7	0.14
E4	14	0.14	1.6	0.015	3.5	0.050	20	0.20	4.6	0.18	3.3	0.032	0.63	0.0052	0.24	0.0021	18	0.12	2.7	0.030	0.38	0.0018	6.7	0.087
F4	15	0.058	1.7	0.015	3.0	0.018	21	0.16	6.3	0.083	3.5	0.022	0.65	0.0037	0.25	0.0016	24	0.26	2.5	0.026	0.38	0.0028	6.3	0.056
G4	18	0.21	1.9	0.015	2.8	0.071	23	0.63	5.6	0.25	3.9	0.054	0.69	0.0045	0.27	0.0097	31	0.95	2.8	0.10	0.35	0.0033	7.0	0.15
H4	19	0.11	2.0	0.014	3.2	0.018	24	0.19	6.2	0.20	4.1	0.025	0.72	0.0052	0.27	0.0049	32	0.39	2.8	0.029	0.34	0.0038	7.1	0.019
I4	22	0.34	2.2	0.035	3.5	0.089	28	0.51	5.8	0.10	4.5	0.043	0.79	0.010	0.28	0.0038	34	0.97	3.0	0.068	0.37	0.0048	7.7	0.16
J4	23	0.54	2.3	0.051	3.3	0.073	29	0.67	7.9	0.28	4.6	0.083	0.83	0.016	0.30	0.0046	36	1.7	3.0	0.083	0.37	0.0034	7.5	0.27
K4	28	0.66	3.0	0.059	3.3	0.075	40	0.85	9.9	0.18	5.1	0.093	0.97	0.0051	0.36	0.022	50	1.1	3.5	0.10	0.36	0.0034	9.1	0.27
L4	29	0.35	3.1	0.051	3.2	0.056	41	0.63	9.7	0.33	5.1	0.080	1.0	0.0039	0.34	0.0085	49	1.3	3.5	0.068	0.36	0.0019	8.9	0.21
M4	29	0.35	3.1	0.051	3.2	0.056	41	0.63	9.7	0.33	5.1	0.080	1.3	0.0071	0.39	0.0068	45	0.94	3.5	0.068	0.36	0.0019	8.9	0.21
N4	32	0.032	3.7	0.012	2.2	0.015	150	0.53	9.5	0.32	5.7	0.014	1.7	0.0044	0.46	0.0057	45	1.2	3.9	0.019	0.41	0.0049	9.1	0.0077
O4	37	0.69	4.2	0.078	3.1	0.088	200	0.97	10	0.43	6.2	0.15	2.1	0.042	0.49	0.0075	63	1.6	4.7	0.13	0.44	0.0059	12	0.36
Quality control parameters																								
MDL	0.06		0.004		0.01		0.02		0.01		0.01		0.002		0.006		0.4		0.01		0.004		0.04	
PQL	0.3		0.02		0.06		0.1		0.6		0.05		0.01		0.03		2		0.05		0.02		0.2	
%RPD																								
G4	1.5		1.8		2.1		1.3		ND		1.2		1.2		12		4.4		3.4		0.48		2.7	
J4	0.40		0.59		0.39		0.51		1.1		0.46		0.44		0.95		1.0		0.53		0.09		1.1	
M4	1.1		1.6		3.3		1.9		18.4		2.2		1.8		0.24		5.3		3.8		2.3		0.94	
Recovery																								
G4	99		97		91		99		NA		87		98		98		58		87		102		84	
J4	84		84		76		84		80		79		87		92		64		73		96		59	
M4	80		79		68		65		104		60		86		93		114		57		93		51	
Ctrl*	NA		99		104		95		NA		NA		101		102		NA		96		101		97	

* Control standard was from ERA, Golden, CO (catalogue number 697, PotableWatR^{TM} Metals); MD, mean deviation of triplicate measurements; m, mean of triplicate measurements; MDL, method detection limit; NA, not applicable; PQL, practical quantitation limit; RPD, relative percent difference.

Table B3. Concentrations of organic compounds measured by GC-MS

SPE fraction	**Both**				**Acids and neutrals**				**Bases**			
Sample ID	**2-oxazolidione**		**N-(2-aminoethy)imdiazolidione**		**N-(2-hydroxyethyl)succinimide**		**N,N'-bis-(2-hydroxyethyl)oxamide**		**N-(2-hydroxyethyl)imidazole**		**Bicine**	
	m	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**	**m**	**MD**
Blank	ND	NA	74	0.55	ND	NA	ND	NA	64	0.7	ND	NA
A6^	ND	NA	400	5.1	35	19	190	4.5	980	23	300	4.8
D4	200	17	300	5.6	380	12	1000	28	380	2.5	ND	NA
E4*	NR	NA	NR	NA	NR	NA	NR	NA	NR	NA	NR	NA
F4	ND	NA	450	8.9	89	4.2	560	10	510	9	ND	NA
G4	85	1.1	430	2	33	1.8	430	12	490	12	170	1.9
H4	90	1.2	440	2.3	29	5.7	430	4.6	560	12	170	2.1
I4	90	1.7	330	4.9	38	7.8	620	16	510	3.1	ND	NA
J4	260	21	340	2.9	240	13	1900	80	820	16	190	1.7
K4	ND	NA	280	2.3	23	2.4	620	22	1100	5	210	0.83
L4	200	13	340	5.3	260	11	1700	76	1400	25	270	12
M4	350	26	370	77	720	17	3400	55	1200	47	200	3.4
N4	100	22	960	26	400	2.9	2100	49	1600	17	160	1.4
O4	100	9.3	590	6.7	110	4.2	910	13	2000	46	200	1.8
Quality control parameters												
%RPD												
Blank	NA		33		NA		NA		<1		NA	
D4	NA		35		83		58		4		NA	
J4	<1		6		3		12		5		NA	
O4	4		4		48		19		8		NA	
Recovery (%, matrix matched)												
D4	103		102		106		25		284		90	
J4	108		125		206		26		894		295	
O4	110		139		118		28		2103		163	

^A6, sample taken from the IBC prior to transferring the absorbent to the pilot plant at Loy Yang; *E4 data is not reported because the internal standard recovery was not satisfactory; MD, mean deviation of triplicate measurements; m, mean of triplicate measurements; NA, not applicable; NR, not reported; RPD, relative percent difference.