

FEASIBILITY OF  
CONTINUOUS  
SCRUBBING OF CO<sub>2</sub>  
FROM AIR AT  
ATMOSPHERIC  
PRESSURE USING AMINE  
TEMPERATURE SWING  
CHEMISTRY

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A thesis submitted in partial fulfillment of the  
requirements for the Degree of Master of  
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by

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## **1 Abstract**

Fuel cells are touted as the workhorses of any future hydrogen economy, intended as decentralised power generators, car engines or for domestic uses. One of the varieties of fuel cells, the Alkaline Fuel Cell (AFC), has had a proven track record in space programmes, and relies on a mature technology developed from the late 50's - but is susceptible to trace amount of carbon dioxide. This project details the feasibility of using an amine/glycol/water solution to scrub carbon dioxide from an air stream from a chemical viewpoint.

Nuclear magnetic resonance (NMR) was used as the primary means of chemical analysis and equilibria studies were performed. The role of oxidation and corrosion were also investigated during the course of investigation.

It was found that the use of an amine/glycol/water solution in a carbon dioxide scrubber was technically feasible and that the role of oxidation is unlikely to be a significant issue. Corrosion studies suggested that the addition of glycol resulted in a decrease in the overall corrosion rate, and that an increase of amine concentration beyond 35% did not significantly increase the rate of corrosion.

## 2 Background

Fuel cells are touted as the workhorses of the future hydrogen economy, intended as decentralised power generators, car engines and for domestic uses. A number of success stories exist, but they are limited to specialised situations, such as the NASA space programme where weight is at a premium, but progress is being made to bring the technology to the public.

One of the varieties of fuel cells, the Alkaline Fuel Cell (AFC), has had a proven track record in the USA's space programme, and relies on a mature technology developed from the late 50's. A major technical problem with AFCs is that any trace of carbon dioxide lowers the efficiency of the cell to the point of inoperability. Previous solutions to the problem have been the use of an oxygen tank, and scrubbing of CO<sub>2</sub> from the air using sodium hydroxide. Neither alternative is easy to implement in the field, and both require constant maintenance and upkeep.

In 2000, a cross-departmental research group of final-year mechanical and chemical engineering students, headed by Dr Susan Krumdieck developed a chemical scrubbing unit that uses a solution of monoethanol amine (MEA), monoethylene glycol (MEG) and water. The scrubber was christened CDOCS, or Carbon Dioxide Continuous Scrubber. While proven to work in a rudimentary manner, much work still needs to be done to deliver a product suitable for reliable operation.

Part of this undertaking in understanding how the scrubber works and in developing design solutions involves answering questions about the absorption and regeneration chemistry, regeneration design and prototype testing.

The main aim of this project is to provide literature and experimental evidence on the technical viability of the Carbon Dioxide Scrubber System (CDOCS).

There are three main questions to be answered:

- 1) Can the system absorb and desorb CO<sub>2</sub> at the MEA and glycol concentrations we are using?
- 2) What are the consequences of operating in a high oxygen environment?
- 3) Will corrosion be a problem and how does it compare to standard practice?

## **2.1 Motivation for a CO<sub>2</sub> scrubber Investigation**

Motivation for the development of a CO<sub>2</sub> scrubber was due to differences from standard applications such as gas sweetening and CO<sub>2</sub> production:

1. Linear flow rate is much higher, due to the design requirement of a compact scrubber.
2. Almost all CO<sub>2</sub> scrubbers are designed to take a gas stream with a high concentration of CO<sub>2</sub>; the AFC system requires a scrubber than can take atmospheric levels of CO<sub>2</sub> and reduce them further.
3. Low pressure operation due to pump limitations, creating a need to reduce the total system pressure.
4. Low energy requirement due to the energy efficiency of the entire AFC system, specifically require a low regeneration temperature.
5. Low maintenance and continuous operation. The AFC systems are envisaged to be located in remote areas, where access for maintenance is limited.

During the course of a postgraduate project undertaken by Jamie Wallace, a scrubber was developed that utilised linear velocities that generated foaming regimes. Although it is an unorthodox operating point for a traditional scrubber design, it does allow for a narrower diameter that reduces construction costs.

### **2.1.1 Amines**

There are a number of methods for CO<sub>2</sub> adsorption in industry. Traditionally, sodium or calcium hydroxide has been used, as it has the benefits of also being hygroscopic, readily available and low cost. This can be done in an aqueous solution using gas-liquid contactors or as a gas-solid system such as soda lime (a mixture of solid calcium and sodium hydroxide) scrubbers. One of the main drawbacks of hydroxide scrubbers is its irreversible reaction, which requires user intervention to periodically replace the hydroxide.

It is for this reason that amines are used industrially. By virtue of their reversible reaction with CO<sub>2</sub>, carbon dioxide systems could now be designed as a closed loop system.

The main workhorse of the carbon dioxide absorption process is MEA. Compared to di and tri-ethanolamine compounds, MEA has the highest CO<sub>2</sub> to amine ratio. This allows smaller liquid pumping rates in gas scrubbers and hence lowers the plant's operating and capital costs.

The main user of amines for gas scrubbing is the natural gas industry, which have to remove excess CO<sub>2</sub> and SO<sub>2</sub> from natural gas sources to concentrate the methane. This process is commonly referred to as 'gas sweetening'

From the lessons learnt in the gas sweetening industry, there are a number of possible drawbacks with MEA, the main two being oxidation and corrosion. Both of these issues will be treated in more detail in the section 'Literature Review of Corrosion and Oxidation'.

Oxidation of the MEA is caused when it is exposed to oxygen at high temperatures. Since this process is irreversible and renders the amine useless, this effectively generates a loss of amine over time. In the gas sweetening industry, this is a very rare as raw natural gas only contains a trace amount of oxygen.

The issues of oxidation serve as a highlight on the differences faced by CDOCS compared to the gas sweetening industry. Firstly, the gas sweetening process, while energy efficient, has more energy available for regeneration. As the natural gas refining plant typically has excess energy available, the most common technique is to use a plate column and regeneration by passing saturated steam counter current to the spent amine solution. Secondly, the composition of the raw natural gas is well defined. Thirdly, and most importantly, the tolerances for CO<sub>2</sub> in the output gas are much higher than what is expected from CDOCS (with a design limit of 10 ppm).

Furthermore, rough design equations from a graduate design project yielded a packed column that was excessively large. The unusually large design is primarily due to the specified high flow rates and low inlet gas concentrations. Traditionally, the maximum linear gas velocity was capped to prevent foaming of the solution and hence blow-through, giving the extremely large diameter. In the AFC scenario, the contact time required for the removal of CO<sub>2</sub> is extremely short (as the amount of change in the CO<sub>2</sub> concentration is from 350 ppm to 10 ppm), making blow-through and bypassing a less important issue than originally thought. As the CDOCS device

can handle a much higher flow rate per unit reactor volume, the size required is drastically reduced.

Corrosion in the plant is practically unavoidable. Heated MEA solution loaded with CO<sub>2</sub> are inherently corrosive (for further details, see *Literature Review of Corrosion and Oxidation*), requiring periodic maintenance and replacement of corrosion affected areas. This has led to the industry practice of limiting MEA concentrations to 10-15%, with various additives experimented with to varying degrees of success.

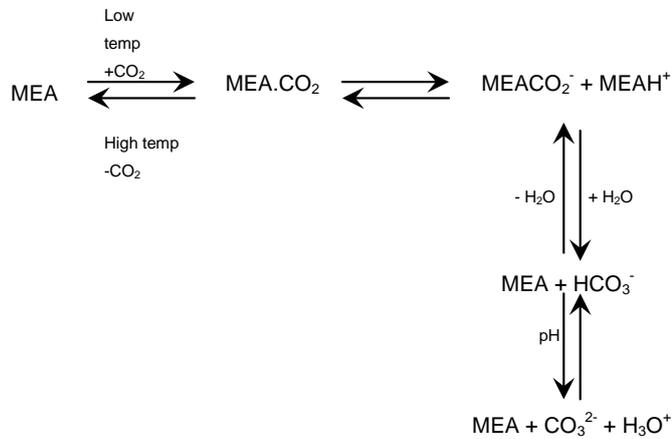
The immediate implication for the CDOCS system at the beginning of the project was whether oxidation would be a problem. Corrosion was not an issue, since the smaller design would allow construction from stainless steel. However, corrosion was a topic of interest for the sponsor company and was thus investigated.

Another reason for this study is the dearth of information on CO<sub>2</sub> absorption into MEA at atmospheric pressure and concentrations. The majority of information on CO<sub>2</sub>:MEA equilibria is at higher pressures closer to those achieved in gas sweetening processes, and the information that is published usually is for low (>20%wt) concentrations. In addition, the data on equilibria at atmospheric conditions is scarce and often at the extreme end of experimental work. The kinetics of the regeneration reaction has not been published at the solution composition used in CDOCS, and this also had to be examined.

It was initially decided to run the column with a high MEA and glycol concentration to reduce liquid requirements. Another question that was required was the operational feasibility and consequence of operating with a system limited by water concentration. A critical part of the reaction involves the hydrolysis of MEA into its protonated form of MEAH<sup>+</sup>, which requires a minimum amount of water to achieve a 1 to 1 molar ratio of MEA to water; posing a question of whether such a system could be technically feasible, let alone practical.

## **2.2 Chemical Reactions**

When CO<sub>2</sub> is first introduced, it reacts with MEA to form a carbamate until equilibrium is reached. The carbamate also exists in equilibrium as a bicarbonate/MEA<sup>+</sup> reaction. The main reactions are detailed in Figure 1.



**Figure 1: Reaction of CO<sub>2</sub> Absorption in MEA (Reproduced from Hook<sup>1</sup>)**

Note that while carbamate formation only allows a 1:2 ratio of CO<sub>2</sub>:MEA, more CO<sub>2</sub> can be absorbed due to protonation of the carbamate – theoretically achieving molar ratios of 1:1. While this can occur, it is usually not significant in primary amine such as MEA (Kohl & Nielsen, 1997), due to the high stability of the carbamate.

During regeneration, the majority of the carbon dioxide is liberated by the bicarbonate/MEA<sup>+</sup> => carbamate => CO<sub>2</sub> mechanism, and some authors (Crooks & Donnelan, 1990) include the direct reaction of HCO<sub>3</sub><sup>-</sup>/MEA<sup>+</sup> to CO<sub>2</sub>.

<sup>1</sup> 'An Investigation of Some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds', Hook RJ, Industrial Engineering Chemistry, 1997, 36, 1779

## 2.2.1 NMR Spectroscopy Methods

It was decided to investigate nuclear magnetic resonance (NMR) as an analytical method. The majority of previous studies have used gas chromatography for species analysis, but it was decided that the technique of chromatography itself would alter the temperature-dependent equilibria too much.

NMR was first predicted in the 1930's as part of interpolation of quantum mechanics. In essence, it predicted that an atomic nucleus with a non-zero spin angular moment has a certain magnetic moment. However, it wasn't until the 1960's and 70's, with the advent of superconducting materials and powerful digital signal processing methods, that it was practical to use NMR techniques for chemical analysis.

NMR works by using an extremely strong homogeneous magnetic field<sup>2</sup> to excite individual atoms. When they fall back to their ground energy state they release energy at specific frequencies characteristic of their position in the molecule.

Subjected to an external magnetic field, atomic nuclei will gain energy in discrete units of energy (quanta). The external magnetic field is then stopped, allowing the nuclei to return to its original (ground state) energy, releasing the excess energy in the form of radio waves at specific frequencies. The energy released is given as:

$$\Delta E = \frac{h\omega_0}{2\pi} = h\nu$$

Where

$h$  = Planck's constant  $6.626 \times 10^{-34}$  J.s

$\omega_0$  = Resonance frequency of the signal (Hz)

$\nu$  = Frequency of radiation emitted (Hz)

The magnetic field can then be adjusted to make the atomic nuclei 'flip' and release radio waves at a specific frequency – this is called the resonance condition. Thus, it is possible to detect how strong the magnetic field needs to be to bring the nuclei to the resonance condition in order to produce a certain radio frequency. Since the

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<sup>2</sup> NMRs typically generate magnetic fields 12 T and higher. In comparison, the Earth's magnetic field is 50 microtesla ( $\mu$ T).

resonance condition is dependent on the neighbouring atoms surrounding the nuclei in the molecule (its chemical environment) is measurable and repeatable, it is possible to deduce the atomic arrangement of the molecule. The chemical environment depends heavily on how the atom is shielded from the external field by the interactions of the atom's electrons with nearby atoms. For the sake of convenience the chemical shift,  $\delta$ , is expressed as parts per million compared to a standard reference chemical:

$$\delta = \frac{(v - v_{ref})}{v_0}$$

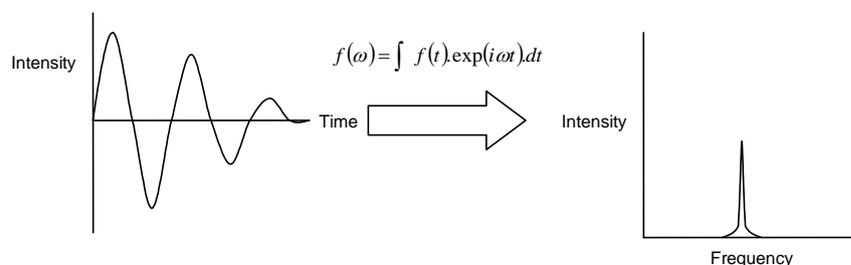
Where  $v$  is the measured frequency,  $v_{ref}$  is the frequency of the reference material, and  $v_0$  is the spectrometer's operating frequency.

This convention has the benefit of being independent on the strength of the external magnetic field used, and the frequency employed. An added benefit is that the area under the curve of a Fourier transformation gives the ratio of atoms in a specific chemical environment. This property of NMR analysis is the basis of the analytical techniques used in this project.

For proton, or hydrogen, NMR methods the procedure is relatively simple. However, the NMR spectra for carbon-13 require a certain amount of time between energising and measurement to allow for spin-lattice relaxation. When a sample is subjected to a high magnetic field, it causes movement relative to the solvent (lattice) that in turn generates its own magnetic field. While this does not affect qualitative readings it does mean the delay time for accurate analytical work must be increased to give the sample time to relax from its over-energised state.

### **2.2.2 Fourier Transformation**

Since the initial raw signal would be waveforms over the time domain, it is necessary to convert it into the frequency domain to view easily the characteristic frequencies.



**Figure 2: Pictorial Representation of Fourier Transformation**

For the purposes of this study, the nucleus chosen was carbon, due to the large amount of hydrocarbon species in the scrubber. However, the most abundant isotope of carbon ( $^{12}\text{C}$ ) has a spin of zero, making it invisible to NMR techniques. However  $^{13}\text{C}$  has similar spin properties to hydrogen (a spin of  $\frac{1}{2}$ ) that, although only comprising 1.1% of all carbon isotopes, allows analysis of carbon compounds. The result is that carbon NMR is not as accurate or rapid compared to proton NMR.

The resultant output of the analysis is a graph with intensity of the energy versus its frequency indexed to a standard (or ppm value) – an example is shown in Figure 3. The integral area under each curve, calculated numerically via an ‘integral trace’, gives the molar ratio of each atom in its chemical environment. One complication with the technique is that rapid equilibria will show up as a single peak even if it is composed of many species. These can be differentiated by that fact that the location of the peak is dependent on the equilibrium point, which means that as the experiment proceeds, the peak shifts too.

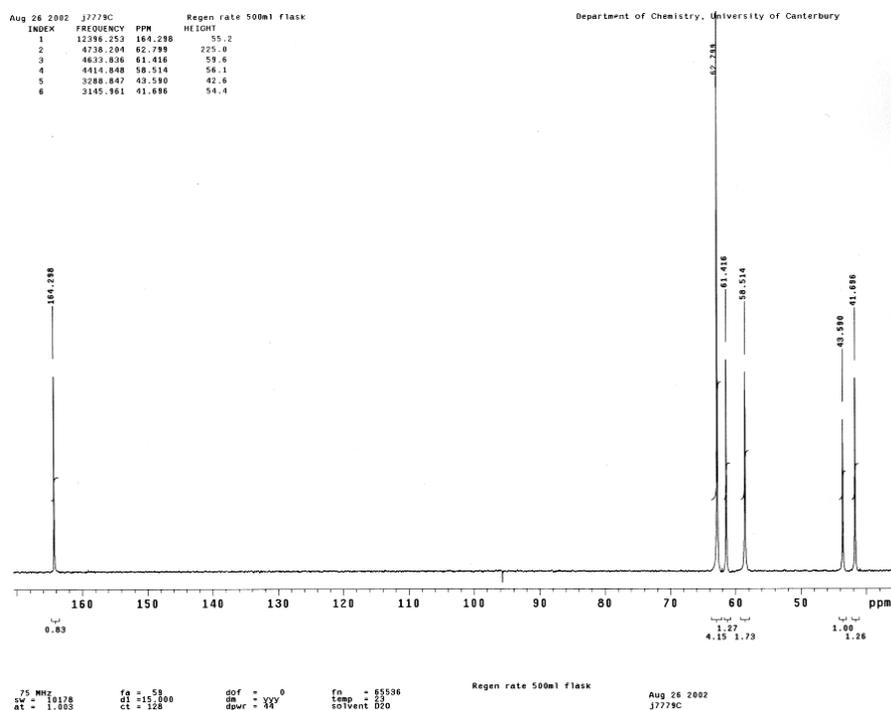


Figure 3: Typical NMR Plot

### 2.3 Corrosion Studies

Studies were performed to investigate the effects of highly concentrated MEA solutions on the corrosion of carbon steel and stainless steels, as well as the effects of differing concentrations of monoethylene glycol in the solution.

Previous studies (see Blanc, 1982; DuPart, 1993) have been done in the temperature region of 80 °C and below, and have typically used MEA concentrations 1 – 5 mol.L<sup>-1</sup> (equivalent to 2.8 – 39% by weight). Currently, the solution in the scrubber is planned to be 50% MEA (8.5 mol.L<sup>-1</sup>) and subject to temperatures as high as 110 –120°C in localised areas of the regenerator. Veawab et al (1999) showed that corrosion increases dramatically with the amount of CO<sub>2</sub> in the system, the amount encountered during typical CDOS operation is negligible. The solution in the regenerator will also be exposed to oxygen, further enhancing corrosion.

The corrosion studies are to examine the effects of amine and glycol concentration at 100 °C by using an electrochemical technique called electrolytic polarization. The polarization method works by applying a known voltage to a test sample immersed in the fluid and measures the current in order to estimate the rate of corrosion.

### **2.3.1 Analysis and Calculations**

**From electrochemical theory, it is possible to deduce the theoretical corrosion current from the experiment by extrapolation in the Tafel region as shown below in**

Figure 4.

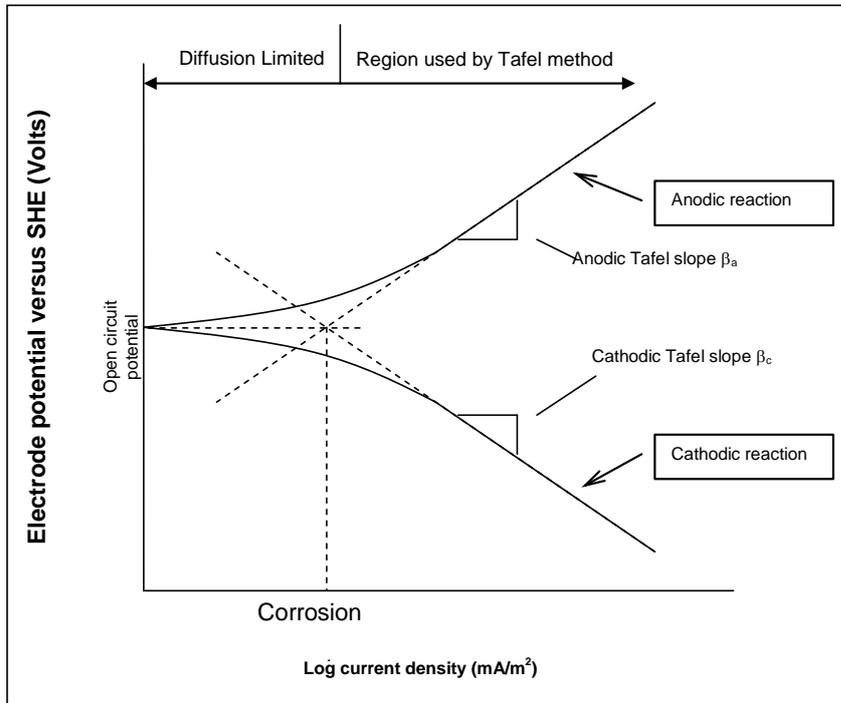


Figure 4: Theoretical Plot of Applied Voltage vs Measured Current

It can also be shown that corrosion penetration (a quantitative measure of corrosion) can be given by:

$$CP = \frac{326.8 \times W \times i_{\text{corr}}}{z \times D}$$

Where:

- CP = Corrosion penetration (mm per year)
- W = Molecular weight of electro active species (g/mol)
- $i_{\text{corr}}$  = Corrosion current density (A/m<sup>2</sup>)
- z = Number of electrons involved in oxidation (metal valency)
- D = Density of metal (kg/m<sup>3</sup>)

## 2.4 Literature Review of Corrosion and Oxidation

### 2.4.1 Introduction

Aqueous monoethanolamine (MEA) is frequently used to scrub carbon dioxide from flue gases, but has well known problems with oxidation. Oxidation occurs due to

oxygen leaking into the closed loop system from traces in the inlet gas, seals, and sample ports.

This section presents a literature review of current research into MEA oxidation and corrosion studies, first separately then discussing the relationship between the two topics.

While the processes of oxidation and corrosion are distinctly separate, they are interlinked; MEA oxidation by-products can include acidic or chelating compounds.

While amine degradation involves many aspects –such as the formation of high molecular weight polymers, and heat degradation – only the affects of oxygen-based degradation will be examined here.

The products of purely oxygen caused degradation fall under two major categories. One, referred to as heat stable salts, are a broad grouping of various compounds that do not reform into their original amine form and carbon dioxide; obviously this is one source of amine loss. The other family of products are organic acids (discussed later in this document), which can contribute significantly to corrosion.

### 2.4.2 Oxidation

The phenomena of oxidation can occur through a number of chemical pathways. Although the presence of iron hastens the process, oxidation will always occur where there is oxygen, MEA and high temperatures.

The US Navy for the application of scrubbing submarine air supplies did initial work on amine degradation (Scheiman 1962). Other researches examined oxidation and found various compounds such as formic acid, ammonia, glycine, glycolic acid, oxalic acid and propionic acid (Holub *et al*, 1998).

A composite oxidation reaction scheme is shown overleaf in Figure 5.

While Kohl and Nielsen (2001) mention that it is possible to form diamines from MEA, they mention that the production of such contaminants are favoured by high regenerator temperatures, high CO<sub>2</sub> partial pressures and high CO<sub>2</sub> loading. These conditions are unlikely to be met in the CDOCS scrubber and can therefore be assumed to be negligible.

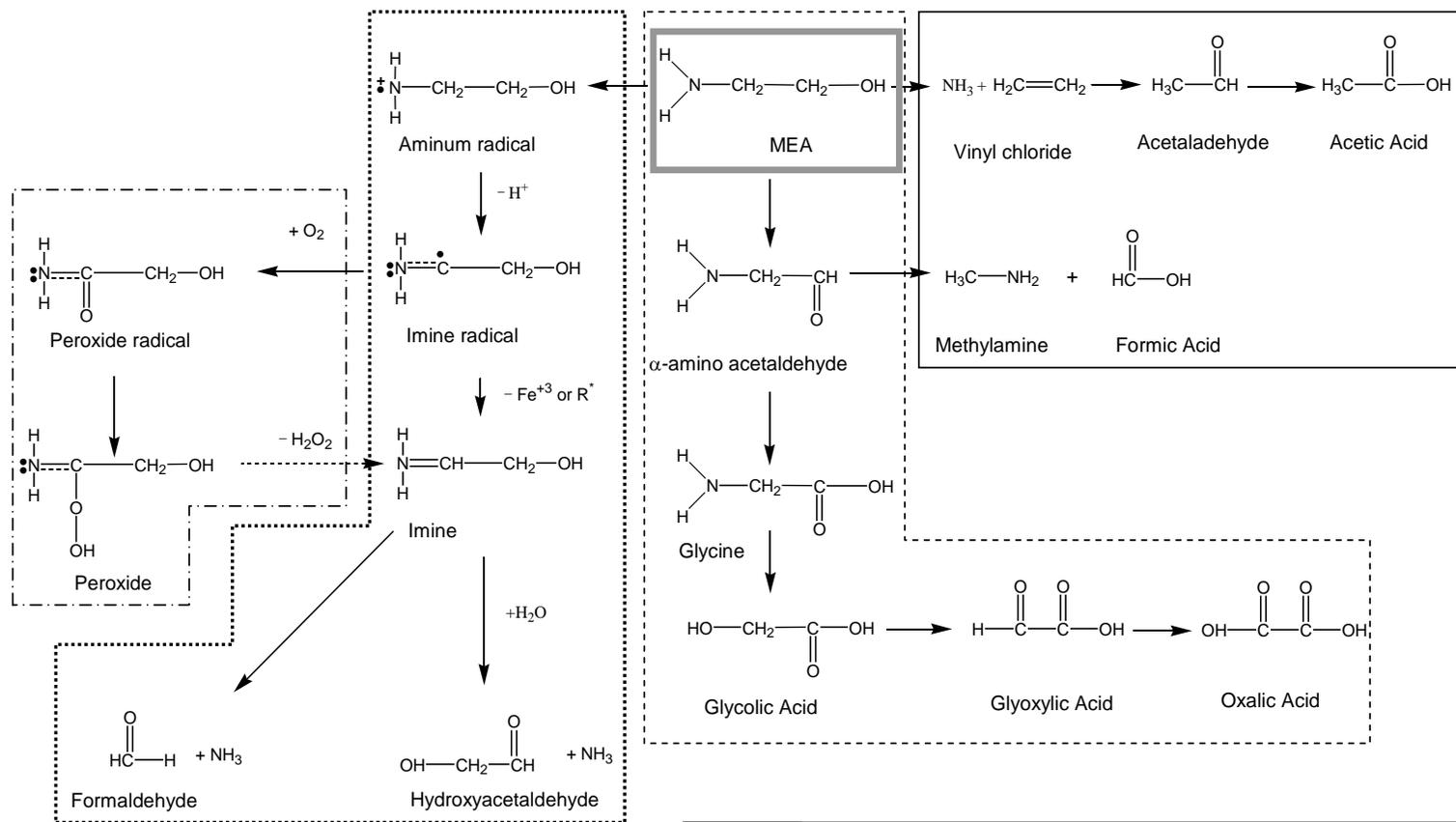


Figure 5: Composite MEA Oxidation Pathway

P.C. Rooney, M.S. DuPart & T.R. Bacon (1996) discussed the possibility of alkanolamines forming heat stable salts due to oxidation. Rooney based their chemical assumptions on a mechanism attributed to Jefferson Chemical that accounts for the formation of glycolic acid, glycine and oxalic acid as found from a US Naval paper<sup>3</sup>. While not explicitly stated, it is guessed from the process description that it was performed in an iron-free environment. All species identified and quantified were done using an ion chromatograph, using standardised samples for comparison.

Experimental runs were done for a number of amines, and samples were taken every seven days for a period of 28 days.

While it was found that CO<sub>2</sub> did result in almost halving the formation of heat stable salts, the rate of salt formation would be insignificant compared to MEA oxidative losses through other pathways.

S. Chi & G.T. Rochelle (2001) examined the rate of ammonia evolved as a measure of the rate of MEA oxidation. A Fourier Transform Infrared analyser was used to measure NH<sub>3</sub> production over 5 – 10 hours; NH<sub>3</sub> production was expressed as millimoles per hour. The work of Chi & Rochelle put forward another oxidative pathway, hypothesising that oxidative compound such as ferrous iron (Fe<sup>+2</sup>) aid the formation of radicals via the formation of imines, leading to acetaldehydes and formaldehyde. Their reaction scheme builds on the work of Hull, and incorporates the role of oxygen rather than iron or organic radical based oxidation.

They found that doses of FeSO<sub>4</sub> into the chemostat resulted in a proportional increase of NH<sub>3</sub> production. They suggested that the addition of Fe<sup>+2</sup> leads to the formation of O<sup>•</sup> radicals, assuming 100% conversion, 3 moles of Fe<sup>+2</sup> lead to 1 mole of OH<sup>•</sup> in turn producing 1 mole of NH<sub>3</sub>. They tested this hypothesis by adding hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which gave a molar ratio of 1:1 with NH<sub>3</sub>, verifying their theory.

Chi also investigates the effects of additives. They found that the addition of 4.5mM and 13mM EDTA (ethylene-diamine-tetra-acetic-acid) to MEA solution with 0.4 CO<sub>2</sub> loading gave a 40% reduction in NH<sub>3</sub> production. The addition to EDTA to a CO<sub>2</sub> free solution had a negligible effect. Bicine [N, N – Bis (2-hydroxyethyl) glycine] was tested in a 7 M MEA/ 1mM Fe<sup>+3</sup> and was found to reduce NH<sub>3</sub> production by 50% with 100mM bicine. While the use of EDTA as an oxidation inhibitor does have technical merit, is highly questionable as EDTA is a highly reactive metal chelating agent that would accelerate iron corrosion.

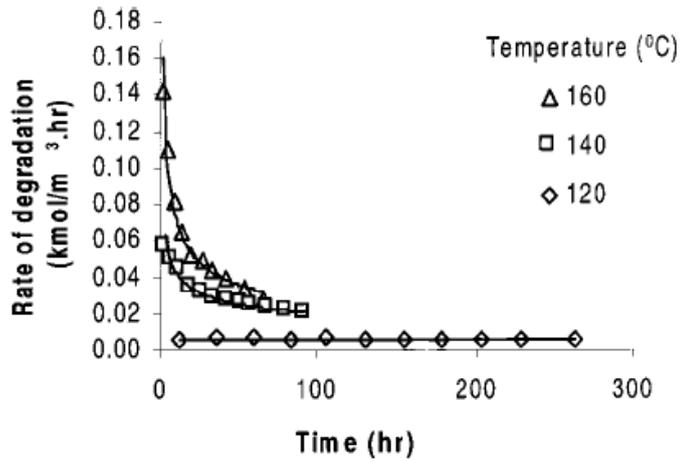
It is also important to note that the proposed reaction mechanism (in the dotted) box generates hydrogen peroxide, which can create more radicals.

Supap et al gets a broader view on alkanolamine oxidation, and examines kinetics of MEA lost and does not quantify by-products or mechanisms of reaction. They propose a power law model based on experimental data collected at the following conditions:

- Temperature: 393, 413 and 433 K
- MEA Concentration: 2, 3, 4, 6, 8, 11 kmol/m<sup>3</sup>
- Oxygen concentration: 241 and 345 kPa

Each variable was done individually, and no experiment involved the manipulation of multiple variables.

It was found that rate of MEA lost was constantly less than 0.01kmol/hr under 120°C, but increased as shown with respect to temperature in Figure 6, below.



**Figure 5.** Instantaneous rate of MEA degradation as a function of degradation time and temperature (initial concentration of MEA = 4 kmol/m<sup>3</sup>, O<sub>2</sub> pressure = 345 kPa).

**Figure 6: From T. Supap et al (2001)**

Their proposed model is:

$$-r_{MEA} = k_0 e^{-\left(\frac{E_0}{RT}\right)} [MEA]^m [O_2]^n \quad \text{Equation 1}$$

Where:

Symbol	Name	Units
$r_{MEA}$	Reaction rate of MEA	mol.m <sup>-3</sup> .hr <sup>-1</sup>
$k_0$	Constant	–
$E_A$	Activation energy	J.mol <sup>-1</sup>
R	Gas constant	J.mol <sup>-1</sup> .K <sup>-1</sup>
T	Temperature	K
m	Reaction order with respect to MEA	–
n	Reaction order with respect to O <sub>2</sub>	–

The values listed by Supap et al are:

Symbol	Value	Error (± abs)
$\ln(k_0)$	12.428	4.899
$E_A/R$	7972	1521
m	1.05	0.18
n	1.51	1.27

A point to note is the extremely high error associated with the oxygen coefficient. While it may indicate fundamental modelling errors, it is likely to be due to the low variation in oxygen concentrations used during testing. As it stands, the large oxygen coefficient indicates that oxidation has a greater dependency on oxygen rather than amine concentration.

The data can be considered valid for the ranges:

<b>Parameter</b>	<b>Range</b>	<b>Units</b>
Temperature	393 – 443	K
Initial MEA concentration	2 – 11	kmol/m <sup>3</sup>
Oxygen concentration (estimated from O <sub>2</sub> partial pressures)	3.154 – 4.293	mol/m <sup>3</sup>

While their data does not give the particular corrosive species present, it does serve as a useful baseline for MEA conversion into other species.

It should be noted that their model does not account for iron present. Chi *et al* (2001) concluded that the rate of MEA oxidation increased fivefold with the addition of 1 mM of iron, by measuring the rate of ammonia produced.

This could also explain some discrepancies between experimental results. While Rooney only produced 825ppm of formic acid at 82°C after 28 days – Blanc *et al* (1982) reported 28,000ppm at a regeneration temperature of 90°C after 30 days.

### 2.4.3 Corrosion

There are many pathways available for corrosion to occur, the main source of corrosion is due to CO<sub>2</sub> loading of the amine solution while a secondary source is from heat stable salts formed from MEA oxidation.

It is thought that the majority of corrosion can be attributed to formation of bicarbonate in the manner as shown below (Veawab et al):

Formation of carbamate:



Disassociation of MEA ion:



Bicarbonate/carbonate equilibria:



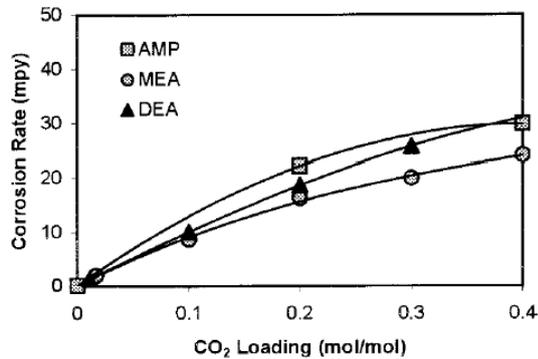
Carbamate hydrolysis:



The bicarbonate then reacts with iron to form iron carbonate.



The work of Veawab et al (1999 & 1999) follows a similar vein to Supap et al, which is not surprising since all the authors also co-wrote the latter. They examine the effects of amine concentration, CO<sub>2</sub> loading and solution temperature of the corrosion rate using an electrochemical corrosion test cell. A calomel reference electrode was used for voltage measurement. It was found that for a 3 kmol/m<sup>3</sup> (~18% by weight) MEA solution at 80°C and maximum CO<sub>2</sub> saturation, the corrosion rate was 145 mpy (millimetres thickness per year).



**Figure 7: Amine Corrosion Experiments (2kmol/m<sup>3</sup>, 80°C, 0% O<sub>2</sub>)**

Unsurprisingly, corrosion was found to increase with amine concentration and temperature. This would be due to increased formation of carbamate (Equation 2) and an endothermic reaction for carbamate hydrolysis (Equation 5) respectively.

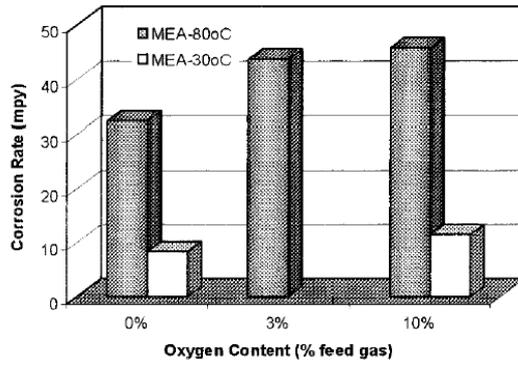
Veawab presented corrosion data for MEA, DEA and AMP (diethanolamine and 2-amino-2-methyl-1-propanol respectively); AMP had a 50% greater rate of corrosion (at 30 mpy) than MEA and DEA. It then follows that most of the corrosion is mediated by the bicarbonate ions; AMP has a much higher rate of carbamate hydrolysis than either MEA or DEA.

The free bicarbonate then forms ferrous carbonate (FeCO<sub>3</sub>), which is then laid down as a passive scale on non-turbulent surfaces. DuPart (1993) suggests that this is laid down as a passive film that prevent further corrosion; as a result corrosion occurs most frequently where high fluid flow disrupts the carbonate layer.

Oxygen also has a significant effect on corrosion through the formation of ferrous hydroxide, leading to precipitation of ferric hydroxide as shown below in Equation 7 and Equation 8:



The results of these experiments are shown in Figure 8.



**Figure 8: Effects of O<sub>2</sub> (2kmol/m<sup>3</sup> MEA and 12%CO<sub>2</sub> in feed gas)**

DuPart (1993) also lists sources suggesting that stress corrosion cracking is particularly important in MEA plants, and stress relieving is crucial to reduce their occurrence. They also advocate the use of mechanical filters to remove all particulates over 5 microns, such as iron precipitates, hydrocarbons and heat stable salts.

#### 2.4.4 Analysis

The general consensus is that products of oxidation accelerate the corrosion process. Rooney et al (1996 & 1996) attempts to quantify this process by spiking a 50 wt% MDEA (methyl diethanolamine) solution with a variety of known oxidation compounds from 180°F to 250°F (82°C to 121°C). These added compounds were:

- Sodium oxalate
- Sodium sulphate (as a control)
- Sodium formate
- Sodium acetate
- Sodium thiosulphate
- Sodium malonate
- Sodium succinate
- Sodium glycolate

The concentrations of the salts ranged from 500 to 10,000 ppm.

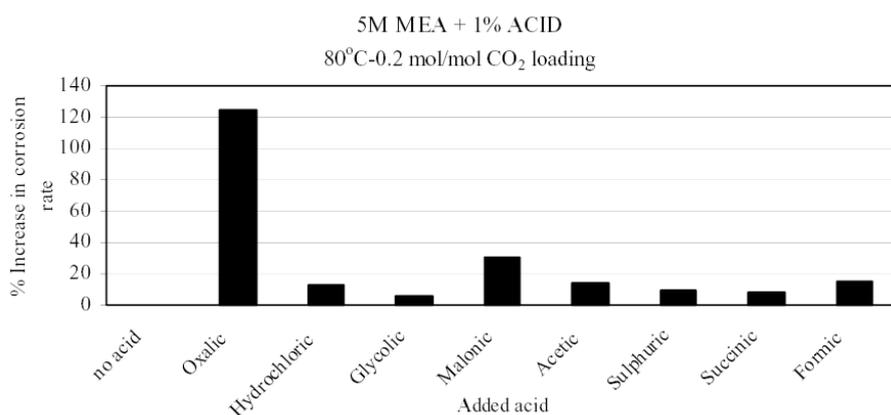
While the experiments were specific to MDEA and the authors did not generalise to other amines, in theory it should give a qualitative indication of the problems caused by oxidation by-products in MEA

Previous experiments, particularly Blanc et al (1982), used electrochemical corrosion cells to directly measure corrosion potentials. According to Rooney, this is a source of uncertainty, as altering the total number of ions in solution by adding oxidation products would also affect the readings taken from the corrosion cell. The authors circumvented this problem by allowing test samples to corrode for 7 days in a reactor, then physically weighing the sample. The rate of corrosion (in mils per year) was back calculated from the density. One shortcoming of the technique is that by scrubbing the sample after the test, the authors would have removed some of the passive film that helps reduce the rate of corrosion; this could have been examined by performing an experimental run over a varying number of days and comparing the results.

The results of the experiment showed that MDEA had negligible corrosion rates without added oxidation products. The worst by-product was oxalic acid, which the authors hypothesised acted as a chelating agent due to non-linearity between

corrosion rate and pH; unlike all the other tested organic additives. The authors then extended their results to include the affects of SO<sub>2</sub> and NH<sub>3</sub> (in the form of sulphurous acid and ammonium hydroxide respectively). Unsurprisingly SO<sub>2</sub> was found to increase the rate of corrosion significantly, but NH<sub>3</sub> was found to cause less than 0.6 mpy at concentrations under 10,000 ppm. This has important implications for interpreting other studies involving oxidation, as experiments that measure only ammonia would be of little use for corrosion rates.

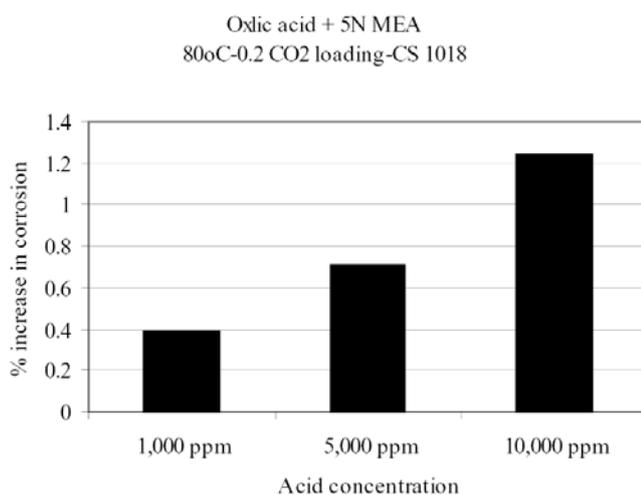
Tanthapanichakoon et al (2002) performed similar experiments, but instead used an electrochemical cell to measure corrosive potentials of a MEA system. The results of the MEA tests on carbon steel follows a similar trend to results obtained by Rooney for MDEA, shown below in Figure 9; the base rate of corrosion is 28 mpy. The principle heat stable salt appeared to be oxalic acid, but unlike Rooney malonic acid aggravates corrosion significantly over other organic acids.



**Figure 9: Rates of Corrosion with Organic Acids at 10,000 ppm (wt)**

When compared to Rooney's (1998) paper that actually gives quantitative information on the organic acids produced, a clearer picture emerges. In general the main products of oxidation are formic acid and acetic acid, while the formation of all other organic acids are collectively less than 10% in total. It highlights importance of taking research material in context; while oxalic acid is the most corrosive by product of MEA oxidation it only represents less than 10% of the total organic acids. Indeed, Tanthapanichakoon does address this in Figure 10, and uses oxalic acid as a representative heat stable salt. Unlike Rooney's results (1996), the effects of heat

stable salts have little effect on corrosion. This is extremely likely due to differences in experimental technique (Tanthapanichakoon used electrochemical cells while Rooney measured mass loss over 7 days) and also due to differing amine type (MDEA has approximately half the corrosivity of MEA).



**Figure 10: Effect of Acid Concentration on Corrosion (Tanthapanichakoon)**

The recommendations of DuPart to reduce corrosion were to remove heat stable salts by a combination of physical filtering then either distillation under partial vacuum or cationic/anionic exchange resins. This has been the main method for amine recovery, and numerous patents have been taken over the years. In particular, distillation has been used in natural gas sweetening processes as it has the added benefit of removing any absorbed water. The use of ion-exchange resins to remove heat stable salts has also been the subject of a number of patents

There also has been interest generated in additives that either prevent the presence of dissolved oxygen ('oxygen scavenging', see US patent number 5,686,016), reduce the incidence of stress corrosion cracking, or to use metal ions such as copper (US Patent 4,690,740) and nickel, (US Patent 4,541,946) to reduce the rate of iron dissolving in solution. Another answer detailed in 6,059,992 is the addition of sodium molybdate (in conjunction with other oxygen scavengers) to create a passivation layer and reduces the rate of corrosion in surface imperfections.

## 2.4.5 Comparison on Corrosion Rates

Author	Rate mpy	Conditions				Other Info
		Temp °C	Pres. atm	Conc kmol/m <sup>3</sup>	CO <sub>2</sub> loading	
Veawab et al (1999)  Note: - Corrosion cell used	5	80	1	1	20%	
	15	80	1	2	20%	
	20	80	1	3	20%	
	23	80	1	4	20%	
	28	80	1	5	20%	
	30	80	1	2	20%	0% O <sub>2</sub> in feed
	40	80	1	2	20%	3% O <sub>2</sub> in feed
	42	80	1	2	20%	10% O <sub>2</sub> in feed
DuPart et al (1993)  Note: - Corrosion cell used	8	60	1	2.493	Sat'd	
	13	100	1	2.493	Sat'd	
	13	98.9	1	2.493	Atm <sup>4</sup>	
	30	115	1	2.493	Sat'd	
	32	98.9	1	4.992	Atm <sup>4</sup>	
	45	120	1	4.993	Sat'd	
Veawab et al (1999)  Note: - This paper discusses AMP corrosion, but included some MEA data.	15.5	80	1	3	0%	
	135	80	1	3	Max	
Tanthapanichak- oon et al (2002)  Note: - Corrosion cell used. Some controversy over accuracy of cells with acidic variation	28	80	1	5	20%	The results of this paper was expresses as % increase in corrosion rate
	33.75	80	1	5	20%	10,000 ppm oxalic acid added.
	32.2	80	1	5	20%	10,000 ppm acetic acid added.

Notes:

- 100% MEA in solution by weight equals 16.62kmol/m<sup>3</sup>, or 16.62 mol/L
- All corrosion data for C1018 carbon steel unless stated otherwise

<sup>4</sup> Atmospheric CO<sub>2</sub> concentration is 360-370 ppm by volume

A literature review of current research into amine oxidation and corrosion was done to investigate the effects of oxidation in long-term operation of the CDOCS scrubber in a high oxygen environment. One paper by Supap et al suggests that the rate of degradation would be as shown in Table 1.

Variable	Value	Units	Variable	Value	Units
Temperature	298	K	Temperature	418	K
MEA conc.	8.8	kmol/m <sup>3</sup>	MEA conc.	8.8	kmol/m <sup>3</sup>
O <sub>2</sub> conc.	8.59	mol/m <sup>3</sup>	O <sub>2</sub> conc.	8.59	mol/m <sup>3</sup>
Degradation Rate	1.5x10 <sup>-4</sup>	mol/m <sup>3</sup> /hr	Degradation Rate	0.3285	mol/m <sup>3</sup> /hr
Degradation Rate	3.6x10 <sup>-3</sup>	mol/m <sup>3</sup> /day	Degradation Rate	7.88	mol/m <sup>3</sup> /day

**Table 1: MEA Oxidation from Supap et al Model**

As the conditions used by Supap, except for oxygen (their highest concentration was 4.2 mol/m<sup>3</sup>), were similar it is likely that the rate of MEA degradation will be accurate enough for the purposes for the initial investigation.

## **2.5 Thesis Overview**

The remainder of this thesis is broken down into three sections:

- Chapter 3, 'Experimental Methods' outlines the experimental procedures used in this investigation.
- Chapter 4, 'Experimental Results' shows the experimental results, and briefly discusses significant findings.
- Chapter 5, 'Discussion' examines the findings in further detail.

### 3 Experimental Methods

#### 3.1 Calibration of NMR Analysis

##### 3.1.1 Aim:

To determine if NMR is suitable for analysis of a CO<sub>2</sub> saturated solution of MEA, glycol and water; and what are the accuracy limits of the technique.

##### 3.1.2 Protocol:

There were three main objective of this experiment:

- 1) To qualitatively identify the scrubber solution
- 2) Determining a suitable delay time setting for the NMR machine
- 3) To establish quantitative analysis of the scrubbing solution

The first pass was to determine if the NMR was suitable for identifying chemical species. In all experiments, the MEA (99%+ purity) was sourced from ASCO, the glycol from the University of Canterbury Chemistry Department and the dry ice from BoC Gases of Christchurch. Eight solutions were made up:

Label	MEA	Glycol	Water	CO <sub>2</sub>
A	X			
B		X		
C			X	
D	X			X
E		X		X
F			X	X
G	X		X	X
H	X	X	X	X

**Table 2: Samples made for Solution Identification**

All solutions were made to approximately 50:35:15 ratios of MEA:Glycol:Water by mass. Partial systems were made in the ratios of the two species only – for example a glycol:water solution has a mass ratio of 35:15.

Peaks were correlated to each chemical species present.

The delay time was estimated by running a relaxation time experiment. The solution used was 50% MEA, 15% Glycol in water with maximum CO<sub>2</sub> loading. The total relaxation time was then found.

To quantitatively measure the species present, a number of solutions were made up to measure the molar ratios of the chemical species present. This was also done to confirm the molar ratio of species present in solution as suggested in *Suda et al. (Chem Letters, p77, 96)*. The solutions made are shown in Table 2, above.

From the corresponding qualitative data, the integrated areas under each peak were correlated to their respective species. The data analysis were performed on the Sun Systems computers in the NMR laboratory and used the following parameters:

Command	Parameter Name	Setting
ins	Integration scaling factor	8500
vp	Variable point	20
bc	Automatic baseline correction	ON

**Table 3: NMR Data Analysis Parameters**

All values were accurate to two decimal places. The values were then transferred manually into an Excel spreadsheet; all calculations and formatting were done using the software package.

### Estimation of Relaxation Time

This was done by software on the "Varian UNITY 300" NMR spectrometer. The solution for estimating the required relaxation time was based in a 50% MEA, 40% MEG solution with maximum CO<sub>2</sub> loading. This was done to take a worst case scenario, eliminating the need to perform a delay time experiment with every solution set. A T1 measurement experiment was performed, with the following results:

Species	Name	Chemical Shift (ppm)	T1	Error
HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup>	$\epsilon$	160.33 to 168.09	1.683	0.054
Glycol	$\alpha$	62.9	0.2449	0.001
MEA	$\beta$	61.3	0.1406	0.005
MEAH <sup>+</sup>	$\beta'$	59.3	0.1724	0.004
MEA	$\gamma$	43.5	0.1336	0.007
MEAH <sup>+</sup>	$\gamma'$	41.6	0.1519	0.003

**Table 4: Results of Delay Time Experiment**

The longest delay time is caused by the rapid equilibrium  $\epsilon$  atom, with a T1 value of 1.683 sec<sup>-1</sup>.

Since the recommended relaxation delay is five times T1 and by definition:

$$\text{Relaxation Delay} = \text{Acquisition Time} + d1$$

For an acquisition time of 1 sec, the d1 value is estimated to be 7.415 sec. This value was henceforth used for all quantitative chemical NMR analysis.

## 3.2 Chemical Composition

### 3.2.1 Aim:

To determine the composition of an aqueous solution containing monoethanolamine, monoethylene glycol and carbon dioxide.

### 3.2.2 Protocol:

A series of solutions were prepared with the compositions shown in Table 5:

Set A	Set B (All with 50% MEA by weight)
10% MEA with maximum CO <sub>2</sub> loading	10% MEG and maximum CO <sub>2</sub> loading
20% MEA with maximum CO <sub>2</sub> loading	20% MEG and maximum CO <sub>2</sub> loading
50% MEA with maximum CO <sub>2</sub> loading	30% MEG and maximum CO <sub>2</sub> loading
	45% MEG and maximum CO <sub>2</sub> loading

Table 5: Sets of Solutions for Quantitative Analysis

In order to achieve partial CO<sub>2</sub> loading, the fully loaded solutions were mixed with the same solution without CO<sub>2</sub>.

Three solutions of MEA and water were made up with of 10, 20 and 50% MEA (solution Set A) by weight and then made up with distilled water. The total mass of solution was typically 250-300g, which was then split into two fractions. One sample was weighted, saturated with carbon dioxide (in the form of dry ice) and then reweighed to measure the amount of carbon dioxide absorbed. The maximum saturation was determined by noting the weight of the solution after adding each pellet of dry ice. Each composition was made by mixing known mass ratios of the saturated solution and the fresh fraction; each had CO<sub>2</sub> loadings roughly increasing by 1/8 from each other. This gave a total of eight solutions with differing amounts of carbon dioxide absorbed.

Four sets solution with the MEA concentration fixed at 50% and glycol concentrations of 10,20,30 and 45% by weight (solution Set B) were used to compare the results of the first experiments and the affects of glycol on the equilibrium state of the solution.

The dilution method was similar to those done on the MEA/H<sub>2</sub>O samples, except that only five samples were produced from each batch of solution.

The ratio of carbamate to MEA was determined by NMR spectroscopy, which in conjunction with the recorded moles of MEA in each sample, gives the moles of carbamate present. These were then compared to moles of CO<sub>2</sub> present. If the moles of carbamate were significantly less than the moles of carbon dioxide, then it could be concluded that it must also be in the form of bicarbonate and/or carbonate. It should also be noted that the amount of bi/carbonate present could not be found directly from NMR due to overlapping peak frequencies.

For each experimental data point, the NMR was set to collect a minimum of 100 transients, with a delay time of 20 seconds to allow for energy relaxation.

In a related experiment, a sample of solution was left for several days sealed with parafilm in a 100ml measuring cylinder. Samples were taken from the top 10mm of solution, middle of the cylinder and the bottom 10mm. The NMR analysis was performed exactly the same way as described previously.

### ***3.3 Viability and Quantitative Analysis of Thermal Regeneration***

#### **3.3.1 Aim:**

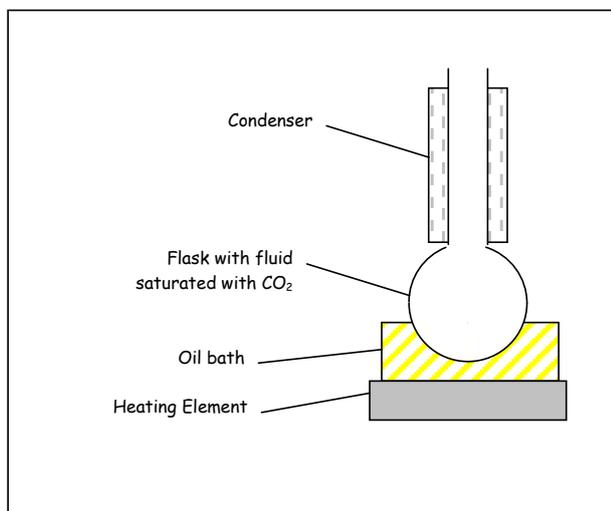
To assess the viability of regenerating CO<sub>2</sub> from a highly concentrated MEA and glycol solution.

#### **3.3.2 Protocol**

One of the questions regarding this study is the kinetics of regeneration. While the reaction between carbon dioxide and a monoethanolamine/water solvent has been well documented, there was still a question of absorption and regeneration with high amine and mono ethylene glycol. The general consensus is that by lowering the vapour pressure, this achieves greater energy efficiency at the expense of greater liquid hold-up and increased capital costs; however there has been no experimental evidence on consequences of running an amine scrubber with a high amine concentration in an oxygen rich atmosphere. There also remains a question on the effects of glycol on amine regeneration and the possibility to utilise fuel cell exhaust gases as a means of purging CO<sub>2</sub>.

Each sample was made up to a total of 100g of solution before the addition of CO<sub>2</sub>. All listed percentage concentrations were done by mass balance. The MEA and monoethylene glycol were sourced from ASCO Ltd, and were assumed to be of high purity.

The experiments were done with various mixtures of MEA, glycol and water by mass and saturated using dry ice purchased by the University from BOP Gases via the chemistry department.



**Figure 11: Regenerator Experiment Setup**

As shown in Figure 11, a stirred round bottom flask is used to contain the liquid while it is heated via an oil bath with a thermostat controlled electrical heating element. All experiments were performed in an operating fume hood in accordance to standard safety practices.

The sample was saturated with CO<sub>2</sub> by introducing dry ice into the solution until the mass balance remained constant. A control sample was taken initially to correlate CO<sub>2</sub> loading from NMR analysis to that obtained by the mass balance. The system was left until it reached room temperature (approximately 20°C), and raised to the required temperature by controlling the temperature of the oil bath. The temperature of the amine was then recorded. Samples were then taken periodically for NMR analysis at predetermined intervals.

The solution was allowed to reach the designated temperature (120°C unless stated otherwise) and held there. It was found that an oil bath at 140-150°C maintained a solution temperature of 120°C. Samples were taken at selected intervals using Pasteur pipettes, and the temperature measured with a -40 to 200°C mercury thermometer with an inherent error of ±0.5°C. A magnetic stirrer was used to keep the solution homogeneous, while silica-based anti-bumping granules provided sufficient nucleation points to form gas bubbles. Bubble nucleation sites were also

found to form on the magnetic stirrer itself and on minor surface imperfections on the glassware. No effort was made to control the air above the solution as it was generated.

An initial sample was taken to record the amount of carbamate present, and the timer started when the heating plate switched on. Samples were taken at 20-40 minutes intervals; samples were taken more frequently within the first 90 minutes. The label name, time and current solution temperature was noted and samples stored overnight in glass containers.

Samples were transferred into 5mm NMR sample tubes along with a deuterium oxide (D<sub>2</sub>O, or 'heavy water') insert. A carbon-13 experiment was set-up and the analysis performed using the following parameters:

Abbreviation	Parameter Name	Value
d1	Total Delay Time	15 seconds
lb	Line broadening	3
fn	Fourier number	64,000
temp	Internal NMR temperature	23°C

**Table 6: NMR Parameters for Sample Analysis**

Since the mixture was relatively simple to interpret and did not contain a large amount of contaminants relative to the concentration of the main species, a minimum 90-100 transients were collected for each run; more transients were collected if time permitted. The purpose of collecting more transients is to reduce noise in the FT plot and obtain integral traces with increased accuracy; it was found that unless the carbamate peak was weak, 90-100 transients were generally enough for a sufficiently accurate measurement within ~0.5%.

## **3.4 Corrosion Investigation**

### **3.4.1 Aims**

To quantify the rate of corrosion in highly concentrated solutions of MEA and MEG, as well as examine the role of copper carbonate as a potential corrosion-inhibitor.

### **3.4.2 Protocol**

A standard corrosion electrode was constructed using araldite to seal a 4mm diameter carbon steel rod into a glass sleeve, so that only the end of the rod was exposed to the corrosive solution. It was found the araldite degraded under high-temperature exposure to amine solution, and it became necessary to recalibrate the effective electrode area using a standard solution of MEA.

The surface was then filed flat and perpendicular to the surface of the sleeve with coarse sandpaper. The electrode was then polished with P1500 grade sandpaper lubricated with water to eliminate surface flaws. The sample was finally rinsed with Milli-Q water and then dried with acetone.

The sample was placed in a corrosion cell with a platinum secondary (counter) electrode and a silver electrode coated with AgCl acting as a pseudo silver-chloride reference electrode. The system was allowed to equilibrate until the open circuit potential of the system remained constant as measured with a voltmeter; it was found that this occurred within 30 minutes.

For the experimental trials that required heating, the vessel was heated by a thermostat controlled oil bath as described in the previous experiment (section 3.3. Viability and Quantitative Analysis of Thermal Regeneration). The temperature of the solution was kept at 80°C to prevent regeneration from altering the CO<sub>2</sub> – MEA equilibrium during the experiment.

A potentiostat (EG&G Princeton Applied Research Potentiostat/Galvanostat, model 273A) in conjunction with a PC for control and data logging used to perturb the system with an applied voltage and record the resultant current. The experiment was then controlled and executed via software supplied with the potentiostat. The linear polarization experiments were set-up with the parameters as specified in Table 7, below.

Parameter Name	Value	Units
Step Time	0.667	mV/sec
Equilibrium Time	3600	sec

**Table 7: Potentiostat Settings for Corrosion Experiments**

The initial and final potentials varied with the experimental set-up and changed as improvements with the experiments were made.

After each change of solution, the apparatus would be rinsed with distilled water, dried and the electrodes re-polished with P1500 grade paper.

Experiments with copper carbonate as a corrosion inhibitor were done by taking a portion of solution in a 50ml vial and adding powdered  $\text{CuCO}_3$  (sourced from ASCO). The mass ratio was defined as the mass of the  $\text{CuCO}_3$  divided by the total solution weight, inclusive of the  $\text{CuCO}_3$ . The solution was then heated to  $45^\circ\text{C}$  in a drying cupboard and shaken until all solids were dissolved into solution. The solution was then used in the same manner as the non- $\text{CuCO}_3$  solutions.

## 4 Experimental Results

### *4.1 Results of Qualitative NMR Analysis*

This section details work done on the MEA/Glycol/CO<sub>2</sub>/water system to identify the chemical species present by experiments detailed in the experimental section. The experimental methods are as listed in 'Calibration of NMR Analysis'.

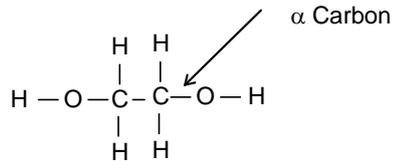
The following figures list a series of NMR spectra on a number of testing solutions. By examining each figure, it's possible to easily identify each chemical compound. Difficulty arises when there are two chemical species in rapid equilibrium, as is the case in the MEA spectra.

### 4.1.1 Glycol – Water System

Species Present:

- Water:

- Monoethylene Glycol:



Note that due to symmetry, the glycol carbons appear as a single peak. There is also no peak for water, since it does not contain any carbon atoms.

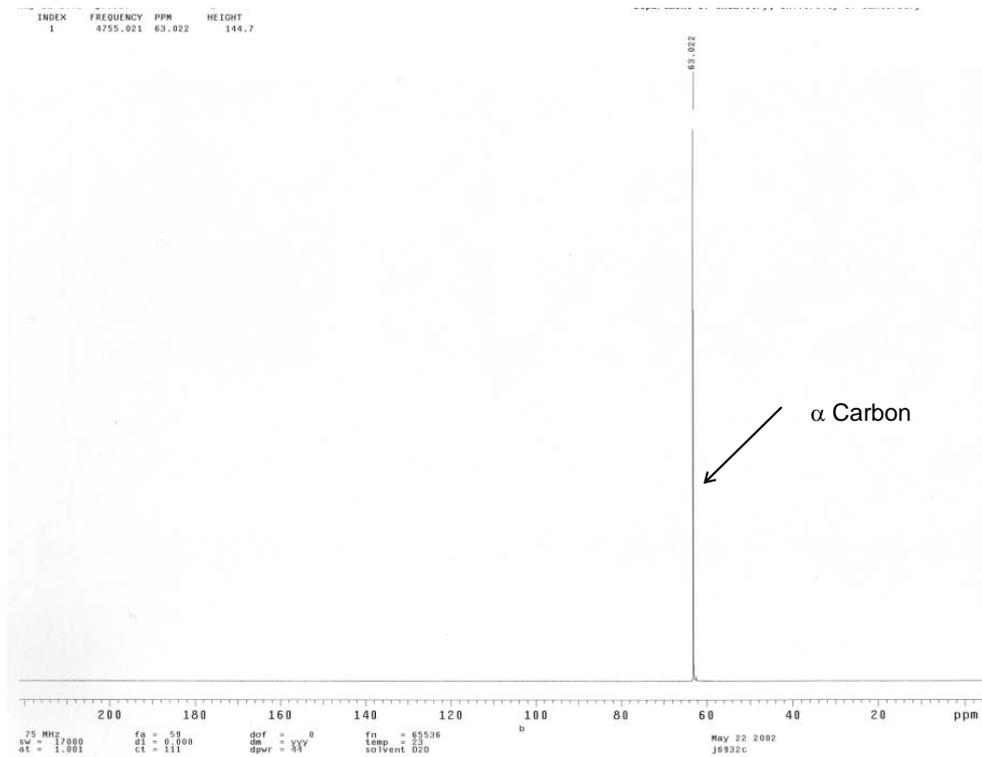
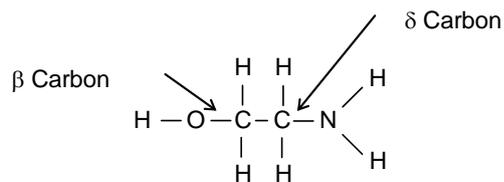


Figure 12: Water - Glycol System

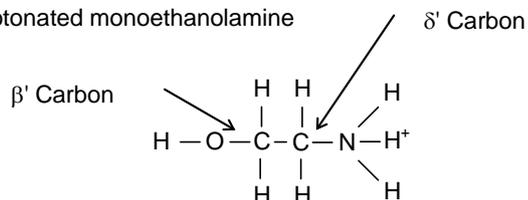
### 4.1.2 MEA – Water System

Species Present:

- Water
- Monoethanolamine



- Protonated monoethanolamine



Note that the  $\beta/\beta'$  and  $\delta/\delta'$  peaks are in rapid equilibrium and thus only show up as a single peak each.

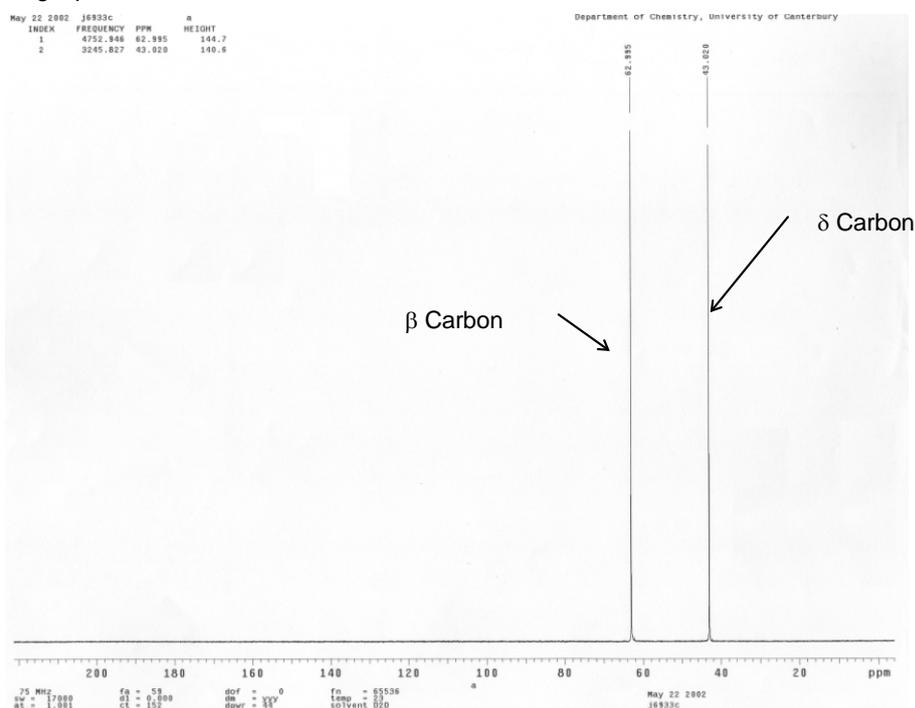


Figure 13: Water - MEA System



### 4.1.3 MEA – Glycol – Water System

Species Present:

- Water
- Glycol
- MEA
- Protonated MEA

Note: The glycol  $\alpha$  peak and the MEA  $\beta$  peak overlap due to their similar positioning in the chemical structure.

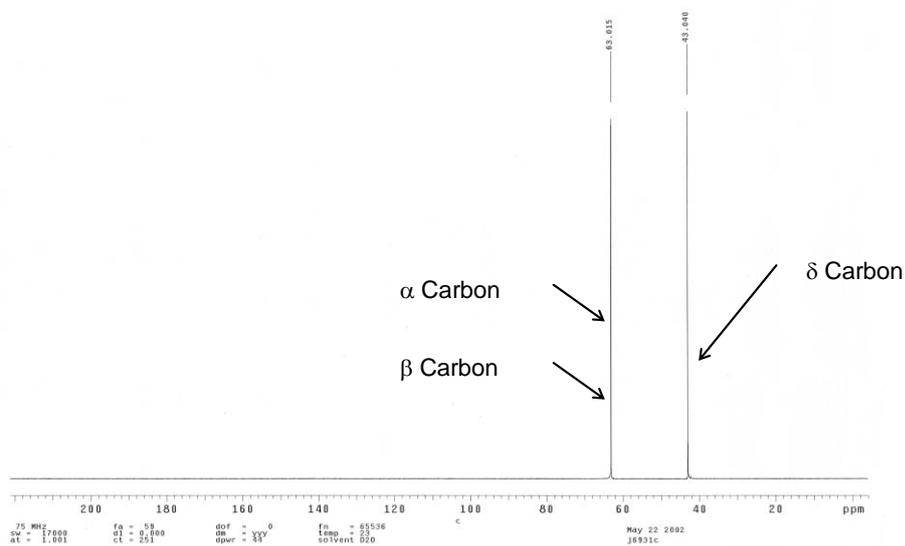


Figure 14: MEA – Glycol – Water System

#### 4.1.4 CO<sub>2</sub> – MEA – Water System

Species Present:

- MEA
- Protonated MEA
- Carbamate: HOCH<sub>2</sub>CH<sub>2</sub>NHCO<sub>2</sub><sup>-</sup>

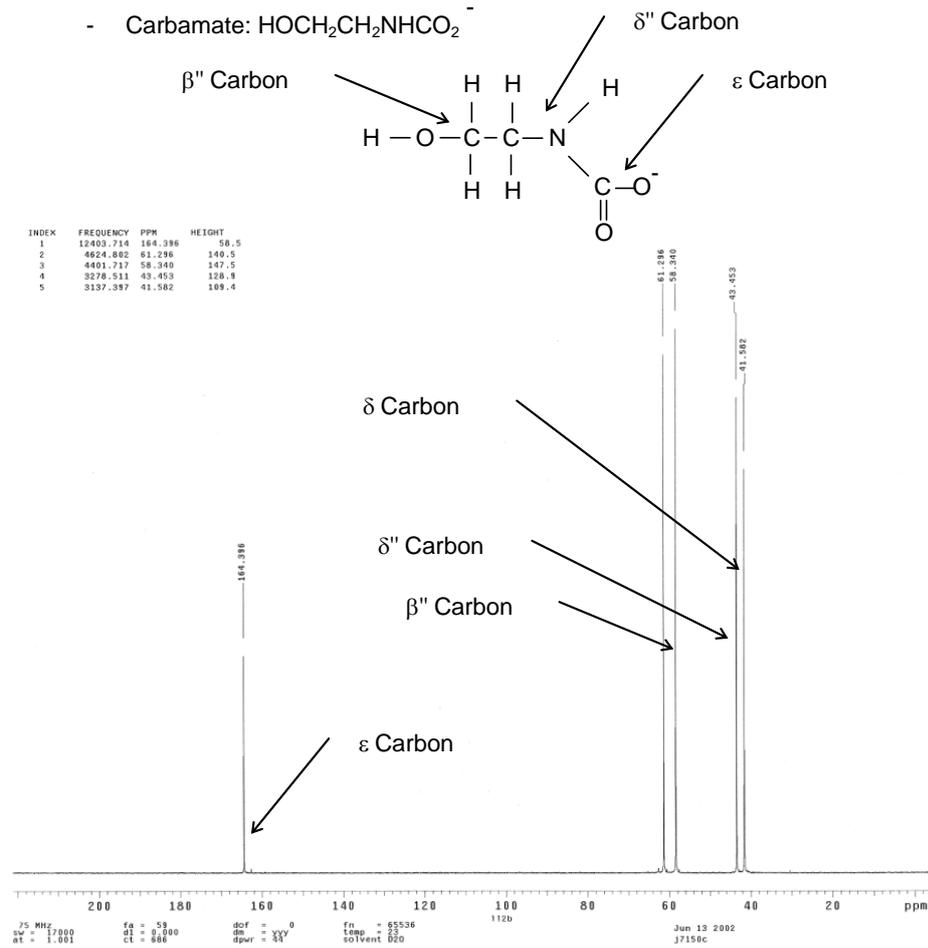


Figure 15: CO<sub>2</sub> – MEA – Water System

The  $\beta/\beta'$  peak varies between 58.5 ppm to 62 ppm depending on the CO<sub>2</sub> concentration. Since the  $\beta$  peak is static at 61.5 ppm, it can overlap making it impossible to perform accurate quantitative analysis based on the  $\beta$  atom.

### 4.1.5 CO<sub>2</sub> – MEA – Glycol – Water System

Species Present:

- Monoethylene glycol
- MEA
- Protonated MEA
- Carbamate

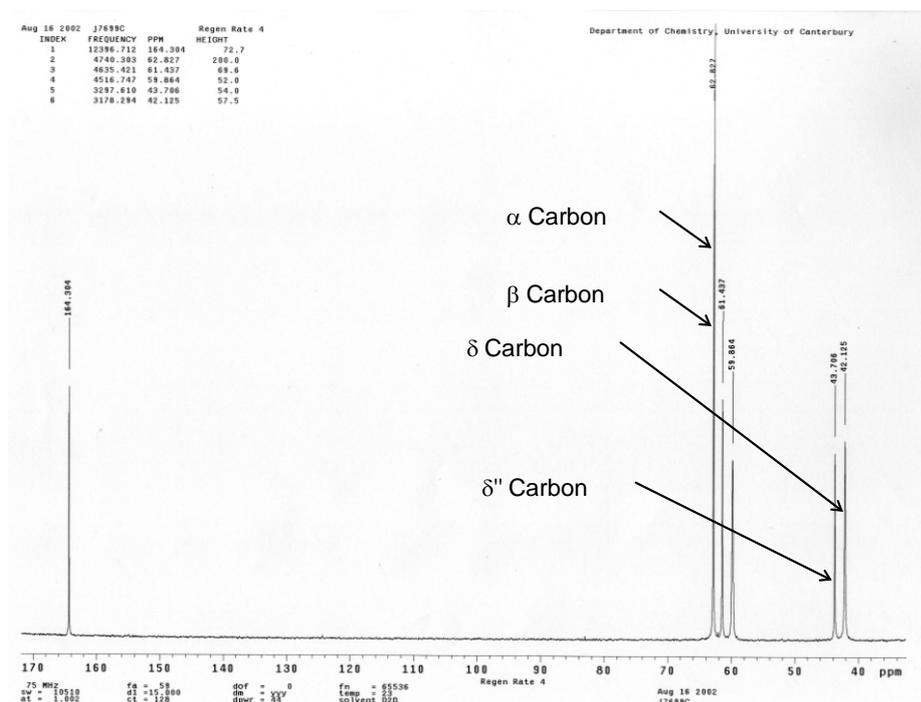


Figure 16: CO<sub>2</sub> – MEA – Glycol – Water System

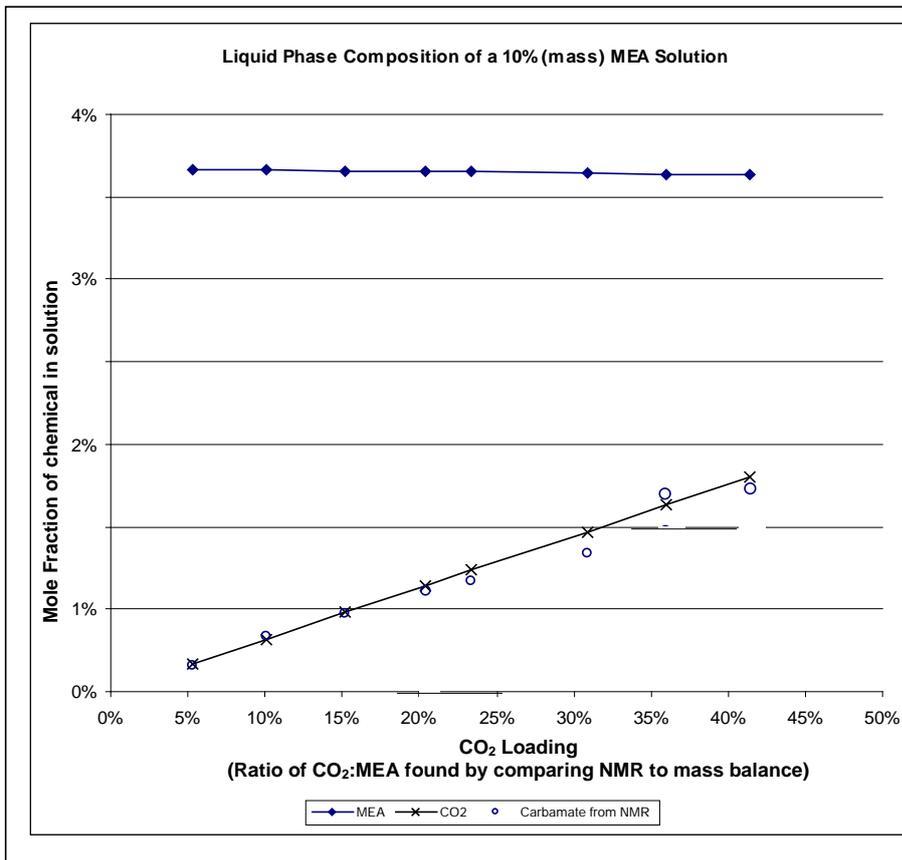
Note that it is almost identical to the previous system, but with the  $\alpha$ -carbon glycol peak overlaid. This gives a proportionally larger peak, depending on the amount of ethylene glycol in the system.

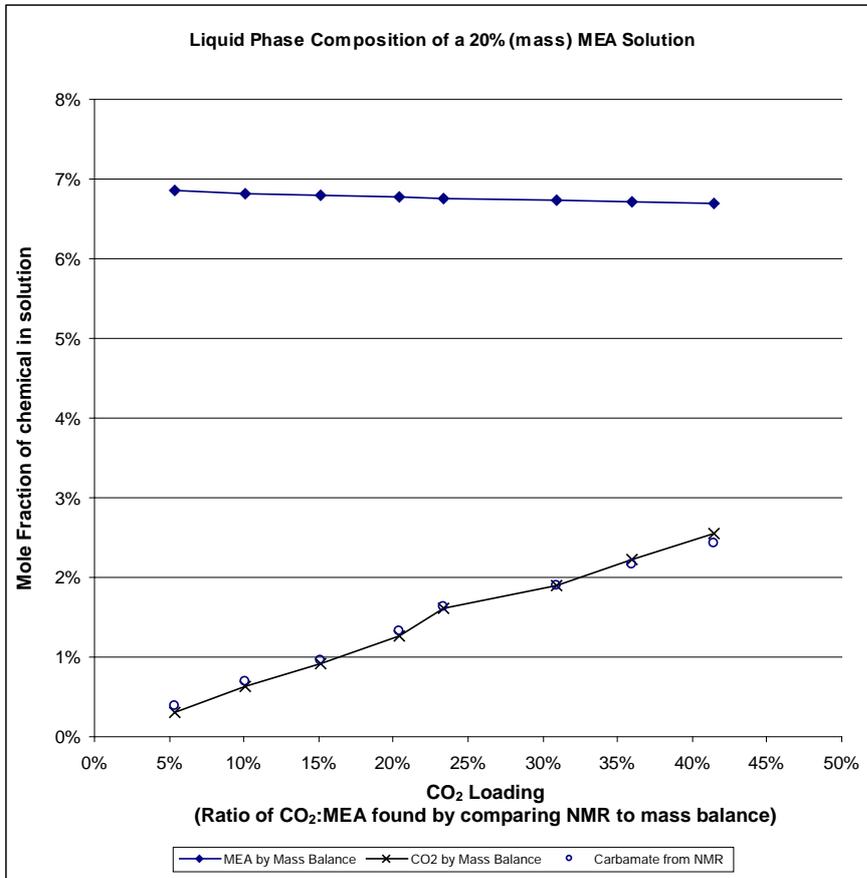
It was found that  $\delta$  and  $\delta''$  peaks gave the most reliable values with minimal error from overlapping peaks.

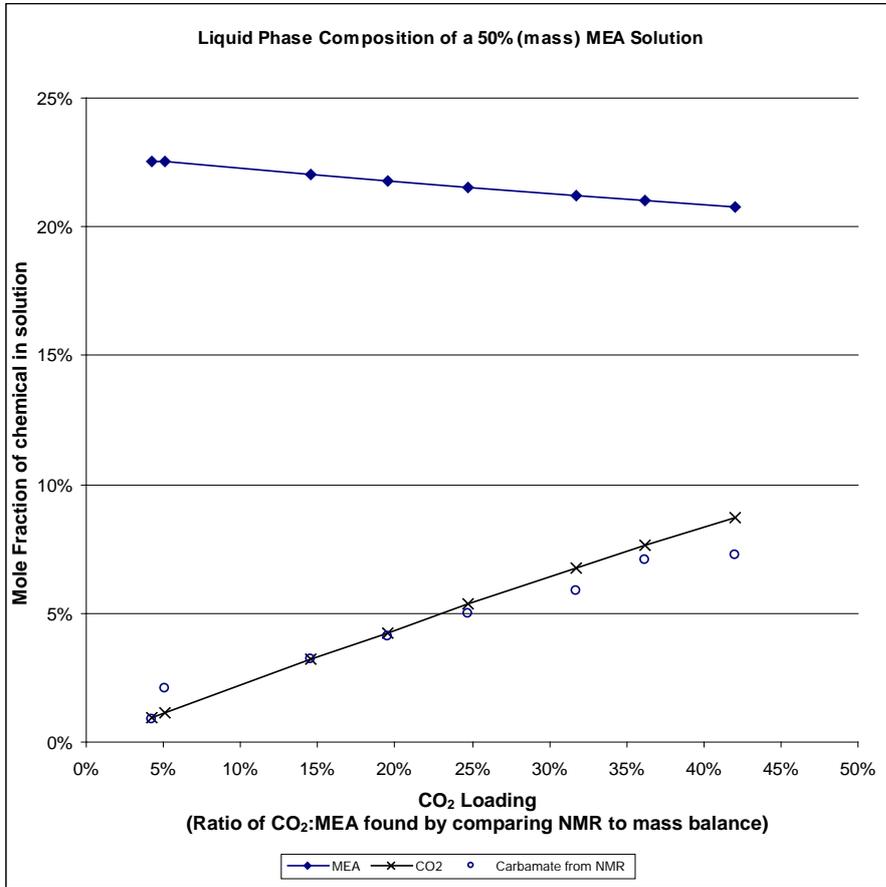
## 4.2 Chemical Composition

These series of figures are to confirm NMR analysis by mass balance. The data points labeled 'CO<sub>2</sub>' is the carbon dioxide in solution calculated by mass balance, while the data points labeled 'Carbamate from NMR' is the amount of carbamate found by NMR analysis in conjunction with knowledge of the amount of MEA in the system.

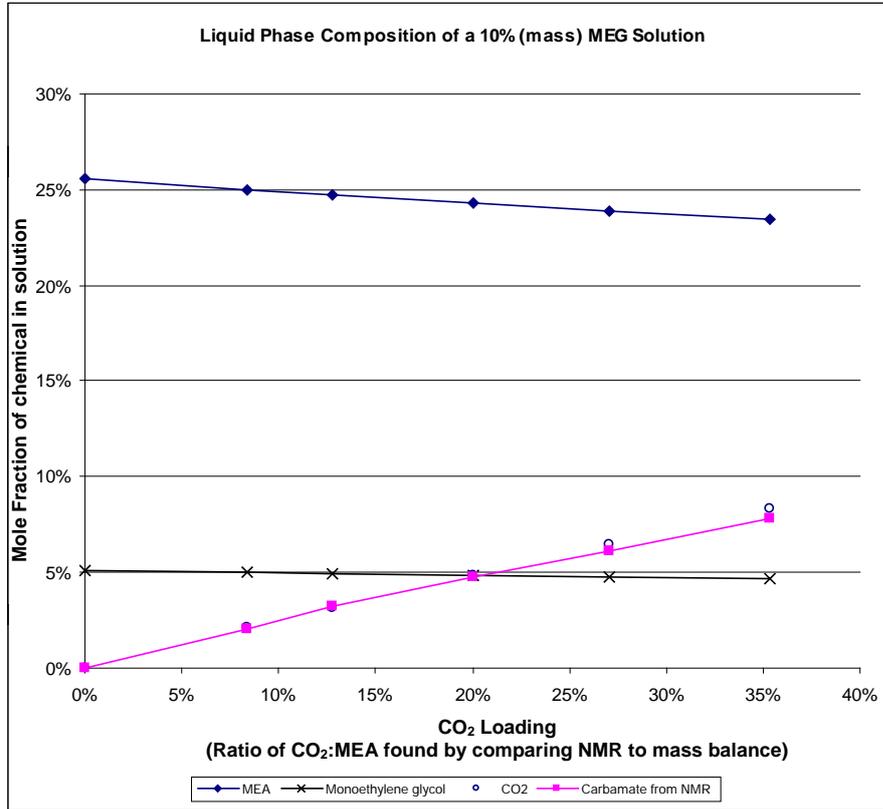
### 4.2.1 Aqueous solutions of MEA and carbon dioxide

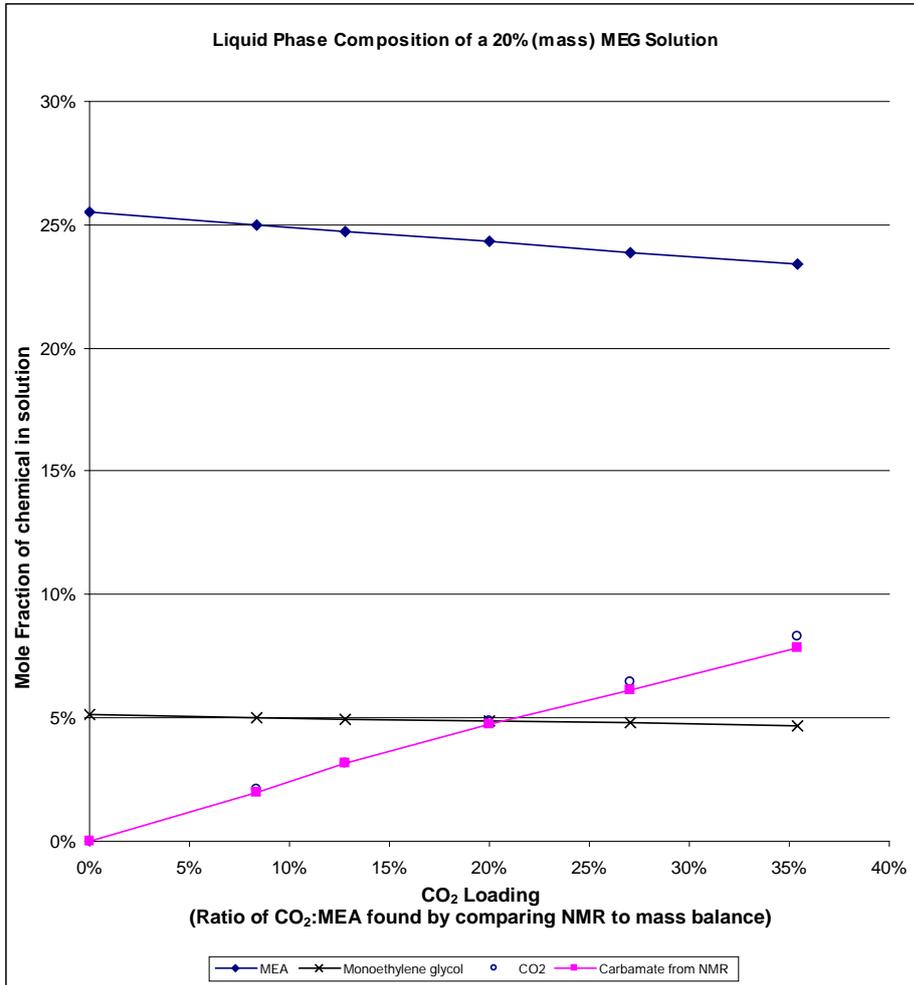


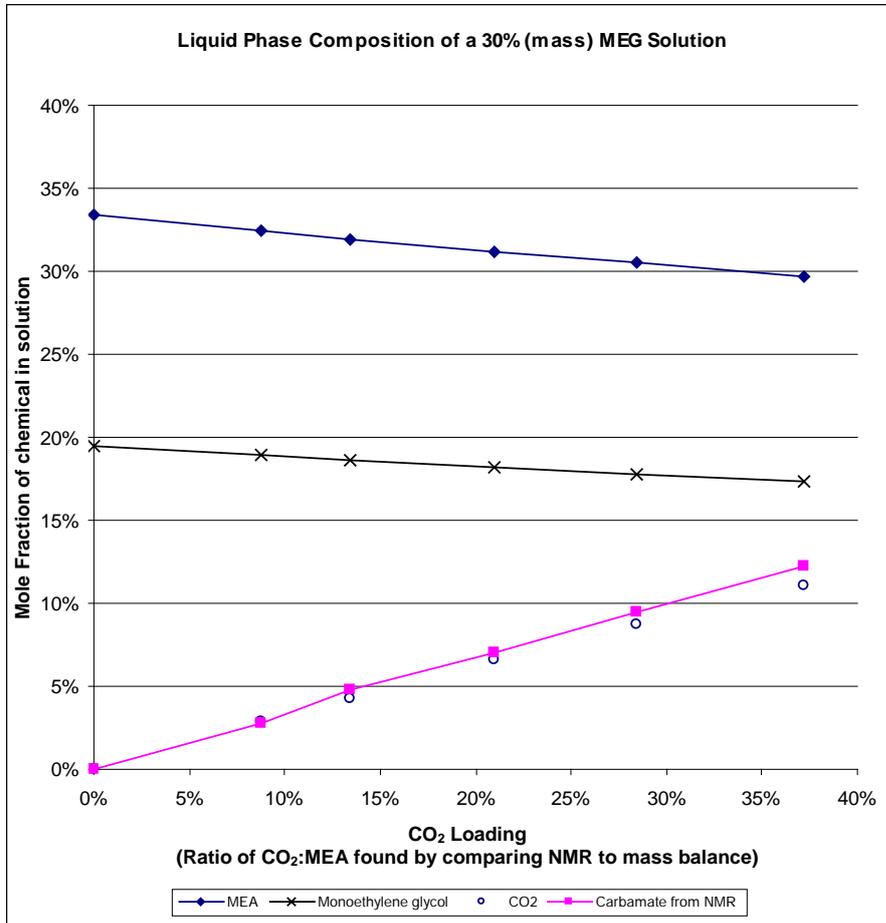


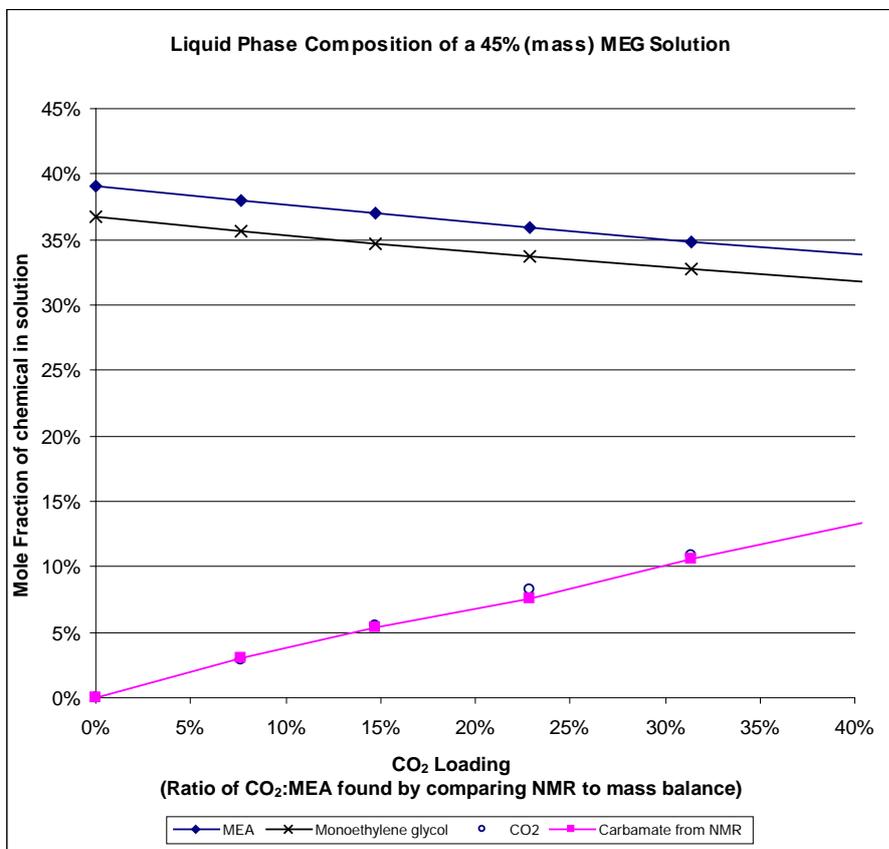


#### 4.2.2 Aqueous solutions of MEA, MEG and carbon dioxide









### 4.3 Regeneration Kinetics

One of the questions in this study concerns the kinetics of regeneration. Although the reaction between carbon dioxide and MEA/water solvent has been well documented, there was still a question of absorption and regeneration with high amine and MEG. The general consensus is that by lowering the vapour pressure, this achieves greater energy efficiency at the expense of greater liquid hold-up and increased capital costs; however there has been no experimental evidence in the literature on consequences of running an amine scrubber with a high amine concentration in an oxygen rich atmosphere.

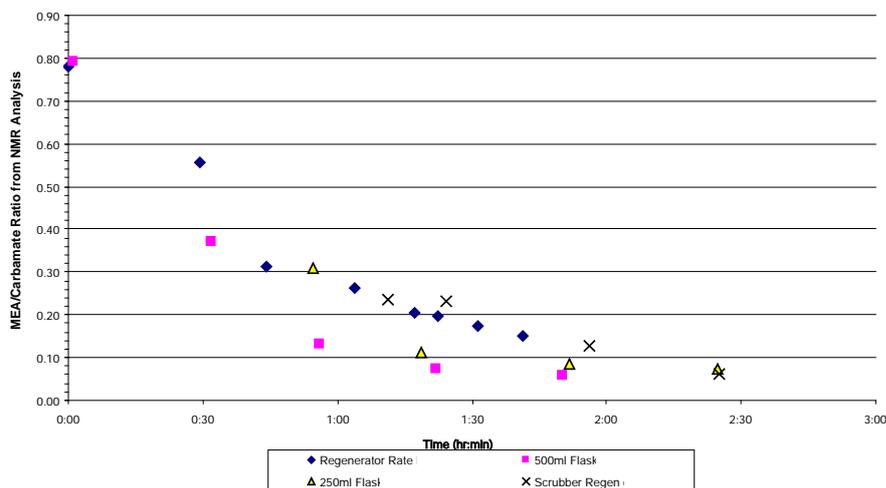


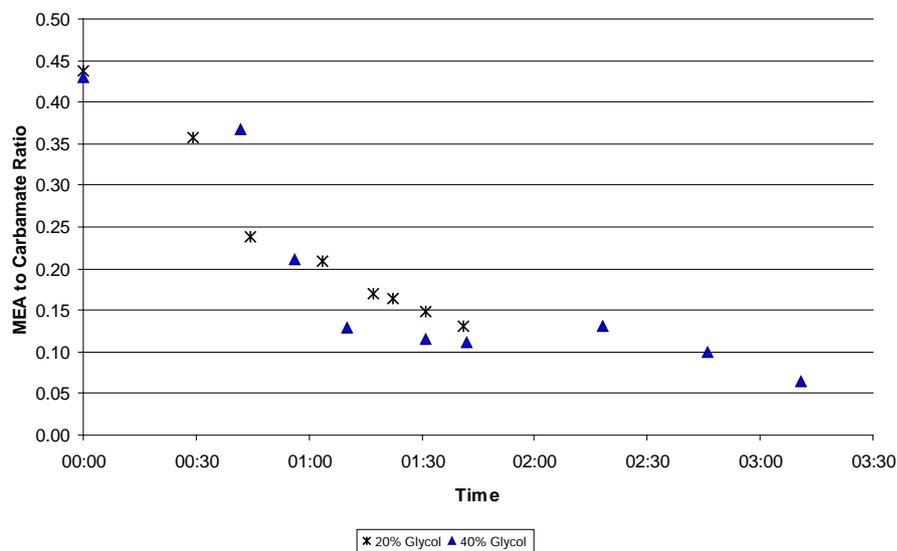
Figure 17: Regeneration Kinetics of CO<sub>2</sub> Saturated MEA/Glycol/Water Solution

The regeneration experiments were done with a 50:20:30 mixture of MEA:glycol:water by mass, and saturated using dry ice. The experimental set-up is shown in Figure 11.

The MEA to carbamate ratio was calculated by comparing the ratios of integrals in the NMR plots. It was found that at ambient conditions, regeneration could be achieved at 100°C, albeit at a much slower rate than could be achieved at 120°C.

The experiments were also conducted in two vessels of different dimensions (500 ml and 250 ml) using 100 ml of saturated solution to investigate the effects of different

geometries on regeneration. The affect of larger liquid surface area for the 500ml vessel could not be detected.



**Figure 18: Comparison of Regeneration Rates with Different Glycol Concentrations**

In order to investigate the effect of glycol-rich solutions on desorption characteristics, a kinetic experiment was performed on a solution containing 40% glycol and 50% MEA (giving a solution with a molar ratio of MEA:glycol:water 40:32:28). A water-cooled condenser was used to minimise water lost through evaporation. The results are compared to those of a solution containing 20% MEG and 50% MEA (Figure 18). From the desorption characteristics it was observed that the two solutions behave similarly.

#### **4.4 Investigation on Operational Variation**

It had been observed that the level of carbon dioxide exiting the CDOCS scrubber (measured using a gas chromatograph) increased dramatically after the solution was left standing overnight.

The solution was therefore examined to determine if the composition changed overnight.

A 50% MEA and 20% glycol solution was saturated with dry ice and then immediately analysed in the NMR to determine the amount of carbamate present. The solution was then transferred to a measuring cylinder and left overnight. Samples were taken after 8 hours from the top, middle and bottom sections in order to ascertain if the solution formed stratified layers overnight. The results are presented below in Table 8. The NMR spectra also did not reveal any unexpected chemical species present.

Sample Label	Carbamate to total MEA ratio
Immediate	0.4044
Top	0.4060
Middle	0.4043
Bottom	0.4063

**Table 8: Results of MEA Overnight Experiments**

From the results, I conclude that there is no significant change in chemical composition overnight.

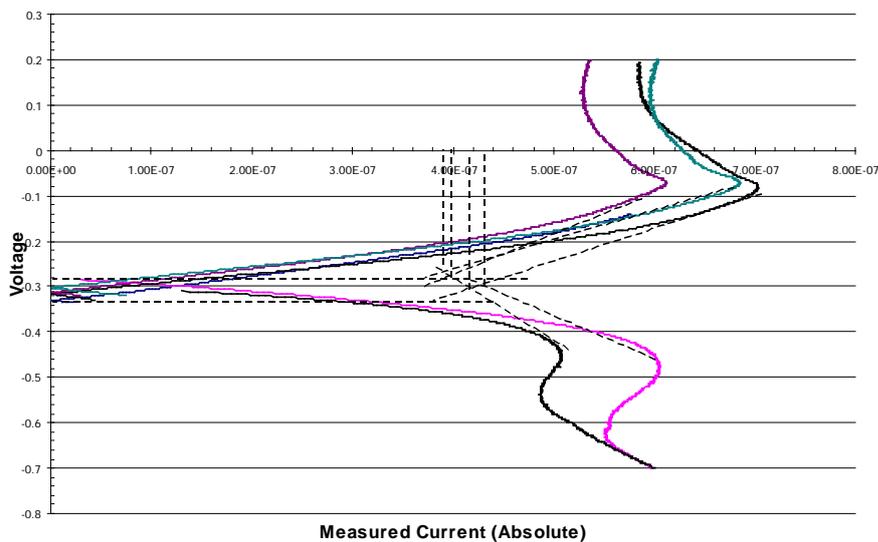
#### 4.4.1 Corrosion Studies

The effects of MEA and MEG concentration on corrosion rates were investigated as described in 'Corrosion Investigation'

#### 4.4.2 Preliminary Results

As shown in Figure 19, below, the actual graph produced from the polarization curves are often more complicated than the idealised plots from theory.

The secondary curves beyond  $5 \times 10^{-7}$  mA are caused by oxide and organic layers forming that inhibit corrosion.



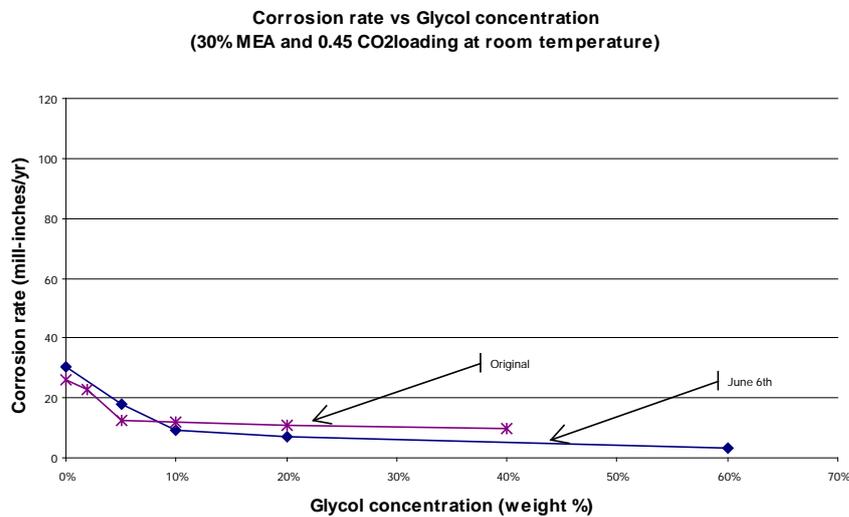
**Figure 19: Example of Preliminary Results for Stainless Steel Sample.**

With the 4 mm sample of austenitic stainless steel provided, the corrosion current is estimated to be  $0.39 \pm 0.03$  mA giving an estimated corrosion penetration of 1.4 mil (1 mil =  $10^{-3}$  inches) per year. Typical corrosion manuals list a 'satisfactory' corrosion rate at 5 mil/yr or less, confirming previous experience of minimal corrosion with the stainless steel packing rings currently being used.

### 4.4.3 MEG Concentration and Corrosion

A series of tests were performed to assess the effect of MEG on corrosivity, the working hypothesis was that a decrease in water in the system would lead to a lower bicarbonate concentration and hence lower corrosion rate.

The results of these experiments (as detailed in 'Corrosion Investigation') are shown in Figure 20 and show the data to be within the margin of error ( $\pm 5$  mmpy) estimated by repeating experimental runs.



**Figure 20: Comparison of MEG Corrosion Testing with Original Electrode and New Electrode**

At present, it does not appear that oxygen contributes significantly to corrosion, rather it is the oxidised by-products of MEA oxidation and degradation that may do so.

As shown in Figure 21, increasing MEA concentration causes a corresponding increase in corrosion, which reaches a maximum corrosion rate at 40% MEA by weight. This is due to the reduction of free water in the system to hydrolyse the MEA into its protonated form as the MEA concentration increases. This would alter the carbamate/bicarbonate equilibrium, stabilising at a maximum value regardless of further increases in MEA concentration. Since the main corrosive agent in the system

is bicarbonate and carbonate, it follows that the rate of corrosion must reach a maximum at very large MEA concentrations, which is consistent with the data shown below.

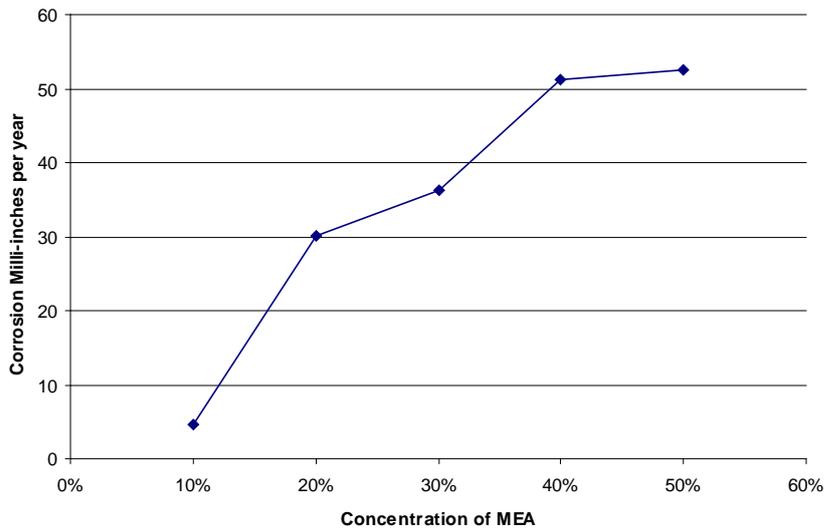


Figure 21: MEA Concentration Vs Corrosion Rate (0.45 CO<sub>2</sub>/MEA, 25°C)

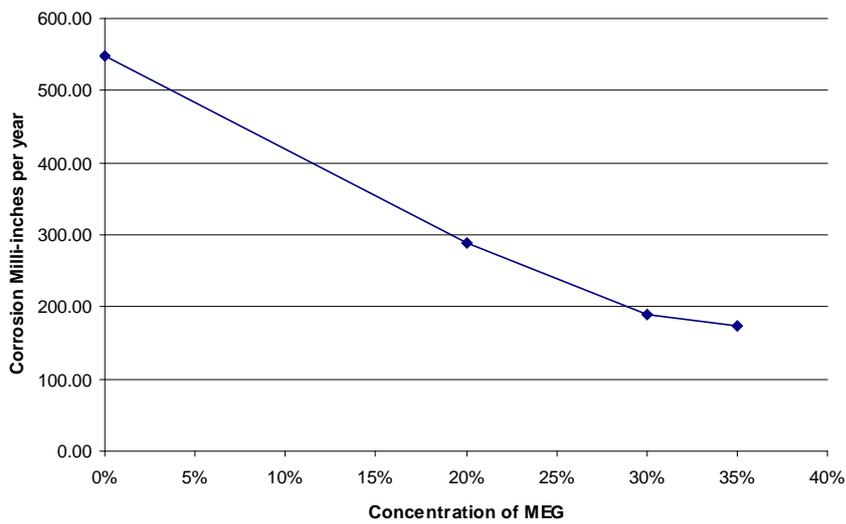
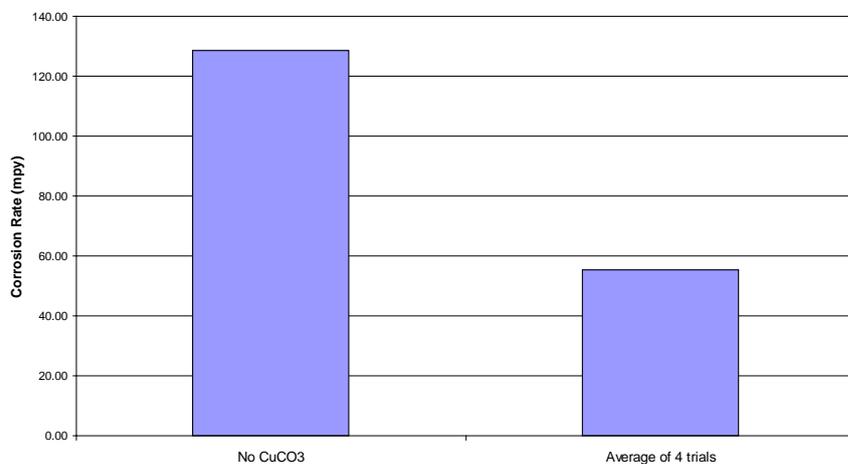


Figure 22: Heated Solution with 50% MEA ((0.45 CO<sub>2</sub>/MEA, 25°C)



**Figure 23: 0.04% CuCO<sub>3</sub> in 10% MEA Solution with CO<sub>2</sub> at 80°C**

Figure 23 shows the effect of copper carbonate as an anti-corrosion inhibitor. While there appears to be a significant reduction in corrosion, it was noted that a layer of copper metal was deposited in the carbon steel electrode. The exact effect of the copper layer is unknown, but is likely to alter the measurement in some way. Without a secondary source for confirmation, it cannot be concluded that copper carbonate is an effective corrosion inhibitor.

## 5 Discussion

### 5.1 The Use of NMR as an Analytical Tool

NMR analysis was decided upon as the method for analysis due to problems with HPGCLC and using mass spectroscopy for quantitative analysis. The decision to use  $^{13}\text{C}$  NMR rather than  $^1\text{H}$  NMR was to streamline the data analysis.

From the data collected in section 4.1, the following species were identified at the following ppm values relative to a deuterium standard:

Species	Value (ppm)
$\text{HCO}_3^-/\text{CO}_3^{2-}$	160.33 to 168.09
$\text{CO}_{2(\text{aq})}$	125.9
Glycol ( $\text{C}_2\text{H}_6\text{O}_2$ )	62.9
MEA ( $\text{C}_2\text{H}_5\text{NH}_2$ )	61.3 & 43.5
MEA $\text{H}^+$ ( $\text{C}_2\text{H}_5\text{NH}_3^+$ )	59.3 & 41.6

**Table 9: NMR Readings for a Carbonated MEA-MEG-Water System**

The values for the MEA and carbamate spectra are similar to those values obtained by Suda (1996).

It is unfortunate that a number of peaks overlapped – however, the  $\delta$  and the  $\delta''$  carbon atoms (see Figure 16) allow reliable chemical analysis. From the ratio of these two peaks it is possible to deduce the ratio of carbamate to total amine. Since some carbon dioxide is lost to form bicarbonate and carbonate, another experiment ('3.2 Chemical Composition') was conducted to assess the error in assuming that all the  $\text{CO}_2$  formed carbamate. This allowed NMR to be used as an analytical tool with an estimated error from the mass balance of 3%.

Analysis of the ratio between MEA and MEA $\text{H}^+$  was done by comparing peak integrals. From the ratio of the  $\delta/\delta'$  and  $\delta''$  integral peaks it is possible to estimate the ratio of carbamate to MEA/MEA $\text{H}^+$ . This was confirmed by mass balance in prepared samples, and also agreed with mass balance calculation performed on a prototype CDOCS within 5%. While the  $\delta/\delta'$  peak shifts due to its rapid equilibria, the integral ratio is still consistent with respect to the ratio of MEA to carbamate.

## 5.2 Chemical Composition Discussion

The increasing difference between carbamate and added carbon dioxide in both samples containing 10% glycol can be attributed to underreporting the mass of CO<sub>2</sub> due to some solution lost due to evaporation caused by the large heat of absorption. The second sample was an attempt to reduce to the solution lost through vapour by using two water-cooled condensers in series, but was deemed to be of questionable usefulness, as there still appeared to be solution lost.

The above results are in line with the results predicted by using the electrolyte-NRTL equation model (Austgen *et al* 1989) and the results published by Suda *et al* (1996) found using NMR spectroscopy. This study was done to confirm the extrapolation used between the 0 to 0.5 CO<sub>2</sub>/MEA molar loading. They both demonstrate that the mole fraction of bicarbonate constitute less than 1% of the molar species in a solution of MEA/CO<sub>2</sub>/H<sub>2</sub>O at a molar ratio of 0.4 CO<sub>2</sub> to 1 mole MEA. The molar ratios are also similar to those predicted, although the mass balance and NMR does not differentiate between the normal MEA species and it's protonated form MEAH<sup>+</sup>.

There appears to be little difference in the absorption rates between 0 to 45% glycol using a 50% mass concentration of MEA. While there was some discrepancy that could be attributed to water vapour lost during CO<sub>2</sub> absorption, the molar ratio of CO<sub>2</sub> in solution appears to be similar regardless of whether the method was NMR or via mass balance. It also means that it is likely that MEA is directly reacting with CO<sub>2</sub> to form carbamate (Austgen *et al* 1989) instead of first undergoing hydrolysis into the Protonated MEAH<sup>+</sup> form; in a solution containing 50% MEA, 45% glycol and 5% water (expressed as mass fractions) the actual molar ratio was 30%, 18% and 42% respectively (the remainder being CO<sub>2</sub>). However, it is likely that the final solution composition will contain a higher percentage of water to prevent dehydration of the gas leading to the fuel cell and lower system complexity.

From this speciation study, it can be concluded that the addition of monoethylene glycol does not significantly affect the basic chemistry of carbon dioxide absorption by monoethanol amine. In addition, the majority of the CO<sub>2</sub> absorbed in solution can be accurately estimated from the carbamate/MEA ratio within 2% of the CO<sub>2</sub> absorbed to total MEA ratio.

### **5.3 Kinetic Data Discussion**

One of the main aims of this thesis was to ascertain whether it was possible to recover CO<sub>2</sub> from a mixture of water-MEG-MEA-CO<sub>2</sub>. The results from '3.4 Regeneration Kinetics' show this to be possible. While it is shown in that CO<sub>2</sub> can be regenerated from a highly concentrated MEA solution (Lin *et al*, 2000) and that MEG can be utilised with minimal affect (Yeh, 2001) no literature has been found that confirms whether or not both situations can be applied simultaneously.

As shown in Figure 7, the effects of MEG on the regeneration rate is negligible within the margin of error. While this is useful for the purposes of regeneration, the amount of MEG in solution has to be weighed against potential problems with absorption and cost of materials.

### **5.4 Literature Review Results**

While it was recognised that oxidation of MEA would have to be assessed, literature from Chi (2001) and Supap (2001) suggested that the rate of MEA oxidation would be negligible. Another factor in the decision not to investigate oxidation was that the CDOCS system is unlikely to be operating with a high concentration of adsorbed CO<sub>2</sub> in solution. The chemical pathways that are thought to occur rely on oxidation through the carbamate, which would be at a lower concentration than those used by both papers.

NMR was used to analysis an oxidized MEA/MEG/Water/CO<sub>2</sub> solution that had been air purged for approximately 100 hours, but it was not accurate enough to determine what the compounds were.

### **5.5 Investigation on Operational Variation**

This was done as part of investigation into unexplained results from the CDOCS testing. There was concern that the solution was settling into segregated layers of differing CO<sub>2</sub> loading. A NMR spectra of a fully saturated MEA/MEG/H<sub>2</sub>O solution taken immediately after agitation to get a homogenous sample. This was compared against three samples taken from various layers after the solution was left for 8

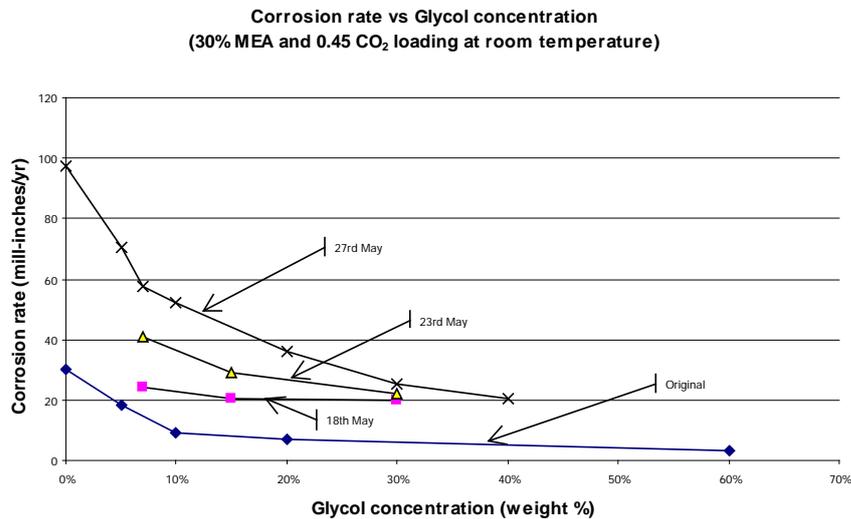
hours. The results show that the solution remains homogenous and does not form stratified layers.

## 5.6 Corrosion Studies

As part of the thesis, a study on the corrosive effects on the MEA/MEG/H<sub>2</sub>O system was performed.

A major problem with the technique used was repeatability. The face of the electrode was carefully prepared to ensure a constant surface area without any flaws which would increase corrosion.

It was found halfway through the project that new data sets taken to fill in gaps in the data points were not consistent. The results are shown below in Figure 24.



**Figure 24: Multiple Runs of MEG Corrosion Testing**

Initially, further plans to increase the resolution of the original data set on the 18<sup>th</sup> May gave the above results. Another set of experiments (May 23<sup>rd</sup>) was then done to confirm the repeatability of the results. Afterwards, the solutions were replaced to eliminate any sources of contamination and another run was performed in 27<sup>th</sup> May.

It was then deduced that the high temperature corrosion testing done after the initial MEG concentration runs had dissolved the araldite resin used to seal the steel electrodes in the glass sleeves. This increased the area of electrode surface exposed

to the solution. Since the corrosion rates depend on the current density (amperes per unit area), this was deemed to be the cause of the increasing corrosion profiles. New electrodes were constructed, and care was taken to rinse off all traces of solution.

The results are similar to data published by Veawab (1999).

## 6 Conclusions and Recommendations

It was found that C<sup>13</sup> NMR can be used as an analytical tool for the investigation of carbon dioxide in monoethanolamine.

Carbon dioxide can be successfully absorbed and desorbed from a highly concentrated MEA solution with glycol and water as the solvent. It was found that, within the margin of error, all the CO<sub>2</sub> was converted into carbamate and not bicarbonate and carbonate.

Corrosion studies suggested that as the concentration of monoethylene glycol rises, the rate of corrosion decreases. It was also found that the corrosion rates of MEA concentrations beyond 35% did not increase significantly. It is recommended that a brief follow-up study using immersion testing be used as a secondary source of confirmation.

Oxidation literature does not suggest that the loss of MEA will be significant. Any further quantitative investigation into the phenomena would have to use HPLC, as NMR is not accurate enough to detect the by-products.

## 7 References

A Aroonwilas, A Veawab, P Tontiwachwuthikul, Behavior of the Mass Transfer Coefficient of Structured Packings in CO<sub>2</sub> Absorbers with Chemical Reaction, 1999, Ind Eng Chem Res, vol 38, pp 2044

A Aroonwilas, P Tontiwachwuthikul, Mass Transfer Coefficients and Correlation for CO<sub>2</sub> Absorption into 2-Amino-2methyl-1-propanol (AMP) Using Structured Packing, 1998, Ind Eng Chem Res, vol 37, pp 569

Austgen DM, Rochelle GT, Peng X, Chen, CC, Model of Vapour-Liquid Equilibrium fro Aqueous Acid Gas-Alkanolamine Systems Using the Electrolyte-NRTL Equation, 1989, Industrial Engineering Chemistry, 28, pp 1060

C Blanc, M Grall, G Demarais, "The part played by degradation products in the corrosion of gas sweetening plants using DEA and MDEA," Proceedings of the 1982 Gas Conditioning Conference.

PMM Blauwhoff, GF Versteeg, WPM van Swaaij, A Study on the Reaction between CO<sub>2</sub> and Alkanolamines in Aqueous Solutions, 1982, Chem Eng Sci, vol 38, no 9, pp 1411

T Bondareva, Kinetics of Regeneration of Monoethanolamine Solutions in Shell-and-Tube Apparatus, 1983, translated from Zhurnal Prikladnoi Khimii, V56, n 11, pp 2516,

Z Cai, R Xie, Z Wu, Isobaric Vapor-Liquid Equilibria of Ethanolamines + Water, 1996, J Chem Eng Data, vol 41, pp 1101

JC Chaptier, Mass Transfer Parameter in Gas-Liquid Reactors with Non-Aqueous Systems, 1981, Symposium Papers – Institution of Chemical Engineers North Western Branch, no 6, sect 5.1

S Chi, GT Rochelle, Oxidative Degradation of Monoethanolamine, Prepared for presentation at the First National Conference on Carbon Sequestration, Washington DC, May 14-17, 2001

L-F Chiu, M-H Li, Heat Capacity of Alkanolamine Aqueous Solutions, 1999, J Chem Eng Data, vol 4, pp 1396

OF Dawodu, A Meisen, Degradation of Alkanolamine Blends by Carbon Dioxide, Dec 1996, The Canadian J. Chem Eng, vol 74, pp 960

OF Dawodu, A Meisen, Identification of products resulting from carbonyl-sulphide-induced degradation of diethanolamine, 1991, J. Chromatography, vol 587, pp 237

D Eimer, H Lidal, O Erga, On Solvent Effects for CO<sub>2</sub> Equilibrium Absorption Using Amines, 1994, Separation Tech, vol 11, pp 739

JH Hirschenhofer, DB Stauffer, RR Engleman, Fuel Cells A Handbook (Revision 3), 1994, US Dept of Energy, Morgan town, West Virginia, USA

PE Holub, JE Critchfield, W-Y Su, Amine Degradation Chemistry in CO<sub>2</sub> Service, 48<sup>th</sup> Annual Laurance Reid Gas Conditioning Conference, 1998, Norman Oklahoma, USA

C-H Hsu, M-H Li, Viscosities of Aqueous Blended Amines , 1997, J Chem Eng Data, vol 42, pp 714

F-Y Jou, AE Mather, FD Otto, The Solubility of CO<sub>2</sub> in a 30 Mass Percent Monoethanolamine Solution, 1995, Canadian J Chem Eng, vol 73, pp 140

ML Kennard, A Melsen, Mechanisms and Kinetics of Diethanolamine Degradation, 1985, Ind Eng Chem Fundamentals, vol 24, pp 129

AL Kohl, RB Nielsen, 'Gas Purification: Fifth Edition', 1997, Gulf Publishing Company, USA

IL Leites, Thermodynamics of the CO<sub>2</sub> Solubility in Mixtures of Monoethanolamine with Organic Solvents and Water and the Commercial Experience of Energy Saving Gas Purification Technology,

Y-G Li, AE Mather, Correlation and Predication of the Solubility of Carbon Dioxide in a Mixed Alkanolamine Solution, 1994, Ind Eng Chem Res, vol 33, pp 2006

SH Lin, CT Shyu, Carbon Dioxide Absorption by Amines: System Performance Predictions and Regeneration of Exhausted Amine Solution, 2000, Environmental Technology, vol 21, pp 1245

SH Lin, CT Shyu, Performance characteristics and modeling of carbon dioxide absorption by amines in a packed column, 1999, Waste Management, vol 19, pp 255

C Mathonat, V Majer, AE Mather, J-PE Grolier, Use of Flow Calorimetry for Determining Enthalpies of Absorption and the Solubility of CO<sub>2</sub> in Aqueous Monoethanolamine Solutions, 1998, Ind Eng Chem Res, vol 37, pp 4126

Various authors, Metals Handbook Ninth Edition, vol 13 Corrosion, Prepared by ASM INTERNATIONAL Handbook Committee, Metals Park, Ohio, USA

D deMontigny, P Tontiwachwuthikul, A Chakma, Parametric Studies of Carbon Dioxide Absorption into Highly Concentrated Monoethanolamine Solutions, Feb 2001, Canadian J Chem Eng, vol 79, pp 137

A Nath E Bender, Isothermal Vapor-Liquid Equilibria of Binary and Ternary Mixtures Containing Alcohol, Alkanolamine, and Water with a New Static Device, 1983, J Chem Eng Data, vol 26, pp370

MS DuPart, TR Bacon, DJ Edwards, Part 2: Understanding corrosion in alkanolamine gas treating plants, May 1993 Hydrocarbon Processing, pp 89

MS DuPart, TR Bacon, DJ Edwards, Understanding corrosion in alkanolamine gas treating plants, April 1993 Hydrocarbon Processing, pp 75

PC Rooney, MS DuPart, TR Bacon, Oxygen's role in alkanolamine degradation, July 1998, Hydrocarbon Processing, pp 109

PC Rooney, TR Bacon, MS DuPart, Effect of heat stable salts MDEA solution corrosivity, March 1996, Hydrocarbon Processing, pp 95

MA Scheiman, 'A Review of Monoethanolamine Chemistry', 1962, US Naval Research Laboratory Report No 5746, USA

J-H Song, S-B Park, J-H Yoon, H Lee, Solubility of Carbon Dioxide in Monoethanolamine + Ethylene Glycol + Water and Monoethanolamine + Poly(ethylene glycol) + Water at 333.2 K, 1997, J Chem Eng Data, vol 42, pp 143

J-H Song, J-H Yoon, H Lee, Solubility of Carbon Dioxide in Monoethanolamine + Ethylene Glycol + Water and Monoethanolamine + Poly(ethylene glycol) + Water, 1996, J Chem Eng Data, vol 41, pp 497

T Suda, T Iwaki, T Mimura, Facile Determination of Dissolved Species in CO<sub>2</sub>-Amine-H<sub>2</sub>O System by NMR Spectroscopy, 1996, Chem Letters, pp 777

T Supap, R Idem, A Veawab, A Aroonwilas, P Tontiwachwuthikul, A Chakma, BD Kybett, Kinetics of the Oxidative Degradation of Aqueous Monoethanolamine in a Flue Gas Treatment Unit, 2001, Ind Eng Chem Res, vol 40, pp 3445

W Tantapanichakoon A Veawab, Heat Stable Salts and Corrosivity in Amine Treating Units, Proceedings of the Sixth International Conference on Greenhouse Gas Control Technologies 2002 (preprint)

Comment [LL1]: Double checked source, and it's listed as 'W', NOT 'P'

A Veawab, Corrosion in CO<sub>2</sub> Capture Unit for Coal-Fired Power Plant Flue Gas, Proceedings of the Sixth International Conference on Greenhouse Gas Control Technologies 2002 (preprint)

A Veawab, P Tontiwachwuthikul, A Chakma, Influence of Process Parameters on Corrosion Behavior in a Sterically Hindered Amine – CO<sub>2</sub> System, 1999, Ind Eng Chem Res, vol 38, pp 310

RH Weiland, M Rawal, RG Rice, Stripping of Carbon Dioxide from Monoethanolamine Solutions in a Packed Column, 1982, AIChE, vol 28, no 6, pp 963

RH Weiland, JC Dingman, DB Cronin, GJ Browning, Density and Viscosity of Some Partially Carbonated Aqueous Alkanolamine Solutions and Their Blends, 1998, J Eng Chem Data, vol 43, pp 378

T Weimer, K Schaber, Absorption of CO<sub>2</sub> from the Atmosphere as a Method for the Estimation of Effective Internal Surface Areas in Packed Columns,

JT Yeh, HW Pennline, Study of CO<sub>2</sub> Absorption and Desorption in a Packed Column, 2001, Energy & Fuels, vol 15, pp 274

X Zhang, C-F Zhang, G-W Xu, W-H Gao, Y-Q Wu, An Experimental Apparatus to Mimic CO<sub>2</sub> Removal and Optimum Concentration, of MDEA Aqueous Solution, 2001, Ind Eng Chem Res, vol 40, pp 898

