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**ENVIRONMENTAL IMPACT OF CARBON CAPTURE
FROM COAL FIRED POWER PLANT BY AMINE ABSORPTION**

FINAL REPORT

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EXECUTIVE SUMMARY

As part of the drive to reduce the emissions of carbon dioxide during fossil fuel power generation, a number of options are being considered by the operators in this sector. These options make up part of the world wide “clean coal” strategy and include pre- and post-combustion technologies. An example of the post-combustion option is the removal of CO₂ from exhaust gases and this can take several forms. The most common currently used technique for carbon dioxide removal from gaseous streams involves its reversible chemical absorption using the amine family of solvents, such as monoethanolamine (MEA). The environmental benefit of such an approach is potentially very large. However the vast body of experience with this approach lies in well known systems with relatively few gases and CO₂ is often the predominant component. The use of this route for high volume, low CO₂ process streams is not fully understood and the likelihood for solvent degradation is high. This may result in two main consequences; decreased absorption efficiency in the system and the generation of undesirable products as a consequence of solvent degradation. The result will be reduced CO₂ capture unless solvent is replaced. Disposal of the spent solvent must not involve any environmental impact and in order to achieve this objective, it is essential to understand the likely degradation products formed. This is the focus of the study reported herein. The report presents the outcomes of a three and a half year project that formed the PhD programme for one of the authors, Kali-Stella Zoannou. During this period two experimental rigs were designed, developed and commissioned in order to explore the effects of gas composition and temperature on the oxidative and thermal degradation of MEA.

It became apparent very early in the study that solvent degradation at process operating conditions normally associated with CO₂ capture with aqueous solutions of MEA was likely to be very low, even at elevated concentrations of oxygen in the flue gas. It was thus necessary to accelerate the degradation rate by operating at elevated temperatures and the opportunity was taken to operate at temperatures higher than those reported in the literature and much higher than those envisaged in practice. The main thrust of the study then became the identification and quantification of the major thermal degradation products in MEA systems and their comparison with other quoted species. In particular the study uniquely enabled the absorption/desorption behaviour of the degraded solvents to be evaluated.

The major conclusions from this work are as follows :

- the rig built to perform repeated absorption and desorption is now available to extend the work performed with MEA with varying gas properties and to include other solvents
- other equipment and procedures are available to perform accelerated solvent thermal degradation studies
- corrosion products were found in the solutions following thermal degradation and an overall corrosion rate of almost 2 mm per year was found at 160°C for the particular stainless steel vessels used

- procedures have been developed to detect, identify and quantify the major MEA oxidative and thermal degradation products
- little deterioration in solvent efficiency for CO₂ capture was observed when operating at standard conditions of absorption and stripping but with oxygen concentrations elevated by a factor of more than three above normal flue gas levels
- even at limited exposure of MEA to oxygen during repeated cycles of absorption/desorption, significant concentration of potentially problematic compounds such as nitrites were found
- thermal degradation at 160 °C for 8 weeks reduced the MEA content by as much as 95% as evidenced both by absorption/stripping behaviour and chemical analysis
- despite the loss of almost all of the MEA by thermal degradation, the remaining solvent still has the ability to remove and release CO₂
- there is some evidence to support the rate of thermal degradation being enhanced as the amount of CO₂ in solution increases, but this effect is low at the elevated temperatures used in the present work
- a range of degradation products have been identified that correspond to those recently cited in the literature
- 1-(2-hydroxyethyl)-2-imidazolidinone, HEIA, is confirmed to be the most stable thermal degradation product
- By searching the available literature it has not been possible to identify any specific environmental or health problems with the major thermal degradation products over and above those routinely encountered with handling mixtures of organic compounds in aqueous solutions and as vapours.

In overall summary, and in order to contribute to the debate concerning possible industrial applications of MEA solutions as means of capturing CO₂ from fossil fuel power generation flue gases, this project has demonstrated that quantitative chemical analyses of the process streams is feasible and that no species have been identified that would give rise to serious concerns regarding treatment of any resulting effluents. Though not fully quantified, the requirement for make-up MEA may not be as serious as predicted by some studies.

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GLOSSARY

MEA	Monoethanolamine
HEEDA	N-(2-hydroxyethyl)-ethylenediamine
HEIA	1-(2-hydroxyethyl)-2-imidazolidinone
IC	Ion Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
microGC	Portable Gas Chromatography instrument
ICP	Inductively Coupled Plasma
TOC	Total Organic Carbon analyser

1 INTRODUCTION

As part of the drive to reduce the emissions of carbon dioxide during power generation, a number of options are being considered by the operators in this sector. These options make up part of the world wide “clean coal” strategy and include pre- and post-combustion technologies. An example of the post-combustion option is the removal of CO₂ from exhaust gases and this can take several forms. The most common currently used technique for carbon dioxide removal from gaseous streams involves its reversible chemical absorption using the amine family of solvents, such as monoethanolamine (MEA). The environmental benefit of such an approach is potentially very large. However the vast body of experience with this approach lies in well known systems with relatively few gases and CO₂ is often the predominant component. The use of this route for high volume, low CO₂ process streams is not fully understood and the likelihood for solvent degradation is high. This may result in two main consequences; decreased absorption efficiency in the system and the generation of products as a consequence of solvent degradation. The result will be reduced CO₂ removal unless solvent is replaced. Disposal of the spent solvent must not involve any environmental impact and in order to achieve this objective, it is essential to understand the likely degradation products formed. This is the focus of the study reported herein.

The aims of this study as initially envisaged were:

1. To build a laboratory-scale gas absorption rig that allows controlled contact of CO₂-laden gases with amine solutions to be investigated.
2. To determine the key parameters that affect the operational lifetime of the absorbent.
3. To examine and determine the range of by-products generated within the system that could contaminate the solvent and affect its operation.
4. A hazard analysis of the health-affecting products.
5. To compare the laboratory scale data with those generated from a pilot-scale plant.

During the course of the project there was a refocusing of the aims, largely driven by the considerable development work required to establish robust analytical techniques for the target degradation products. For that reason the outcomes are related principally to the first three aims. It became apparent very early in the study that solvent degradation at process operating conditions normally associated with CO₂ capture with amine solutions was likely to be very low, even at elevated concentrations of oxygen in the flue gas. It was thus necessary to accelerate the degradation rate by operating at elevated temperatures and the opportunity was taken to operate at temperatures higher than those reported in the literature. The main thrust of the study then became the identification and quantification of the major thermal degradation products in MEA systems and their comparison with other quoted species. In particular the study uniquely enabled the absorption/desorption behaviour of the degraded solvents to be evaluated.

2 EXPERIMENTAL

2.1 Materials

All the chemicals used in the laboratory work are listed in Table 2.1

Table 2.1 Chemicals and associated materials used and their sources

Chemical	Function	Supplier
Paraffin oil	Oil bath medium	Fisher Scientific
Ethanolamine 99.5%	CO ₂ solvent	Fisher Scientific
SulfaVer 4 pillows	Sulphate analysis	HACH [®]
NitraVer 5 pillows	Nitrate analysis	HACH [®]
NitriVer 2 pillows	Nitrite analysis	HACH [®]
OnGuard II H cartridges	IC sample pre-treatment	Dionex
TraceCERT Nitrate standard	Chemical analysis by IC	Sigma-Aldrich
TraceCERT Nitrite standard	Chemical analysis by IC	Sigma-Aldrich
Potassium nitrite 97%	Chemical analysis by IC	Acros Organics
Sodium nitrate	Chemical analysis by IC	Fisher Scientific
Sodium Formate 99% AR	Chemical analysis by IC	Fisher Scientific
Potassium Acetate 99% AR	Chemical analysis by IC	Fisher Scientific
Potassium Oxalate 99.5% AR	Chemical analysis by IC	Fisher Scientific
2-Oxazolidone 98%	Product of degradation	Sigma-Aldrich
1-(2-Hydroxyethyl)-2-imidazolidinone	Product of degradation	Sigma-Aldrich
N,N-(2-Hydroxyethyl)formamide	Product of degradation	Sigma-Aldrich
N-(2-Hydroxyethyl)ethylenediamine	Product of degradation	Sigma-Aldrich
17% O ₂ , 15% CO ₂ in N ₂	Micro-GC calibration	Scientific and Technical Gases
Diethyl Ether	GC-MS analysis	Fisher Scientific

All aqueous dilutions where necessary were performed with deionised water.

2.2 Analytical equipment

Ion Chromatography, IC

The IC system was used for the analysis of the major MEA oxidative degradation products. It was the Dionex ICS-2000 fitted with the IonPac AS11-HC anion exchange column with a conductivity-dependant detector.

Gas Chromatography – Mass Spectrometry, GC-MS

The GC-MS system was used for the analysis of MEA and its major thermal degradation products. All work was performed on a Perkin Elmer CLARUS 500 GC-

MS using a range of columns and instrument conditions. Only the results with the Rtx 5 Amine column purchased from Restek will be reported herein.

The Micro Gas Chromatograph, micro-GC

The micro-GC (Varian CP-4900 running their Galaxie software with a thermal conductivity detector and the packed column M5A BF with helium as a carrier gas) was used to measure CO₂ concentrations at the exit of the gas absorption/desorption rig described in the following section.

Inductively Coupled Plasma Spectrometry, ICP

For the analysis of the corrosion products an ICP system was used. The instrument used was the Perkin Elmer Optima 2100DV ICP-OES running the WinLab 32 software

Carbon Contents of Aqueous Solutions

The CO₂ molar loadings of the MEA samples were determined by means of the inorganic carbon measurement with a TOC instrument. These measurements were made with a Total Organic Carbon Analyser TOC-500(A) by Shimadzu using the TOC-control-V software.

Colorimetric Determinations of Anions

These were performed with the HACH portable data logging colorimeter DR/890

2.3 Experimental Rigs

2.3.1 Gas Absorption / Desorption Rig

This system (see Figures 2.1 and 2.2) was built so as to allow repeated cycles of absorption and stripping to be applied to different solvents. The purpose of this rig was to assess the performance of different solvents and the key parameters that affect their operational lifetime. The principal components were all commercially sourced and are listed as follows:

1. A gas feed system with three large gas canisters for pure CO₂, O₂-free N₂ and air together with their regulators, and in the case of CO₂ an in-line heater
2. Three pneumatic in line non-return valves, 1/4"
3. Four rotameters, two for CO₂ and two for N₂, purchased from Fischer Scientific Ltd with the following specifications:
 - Flow meter air/nitrogen variable 0.1-1.2 L/min Influx (product no FJC-625-035V)
 - Flow meter air/nitrogen variable 0.02-0.25 L/min Influx (product no FJC-625-015E)
 - Flow meter carbon dioxide variable 10-100 cm³/min Influx (product no ENGFIS1-CO₂)
 - Flow meter carbon dioxide variable 50-750 ml/min Influx (product no ENGFIS14-CO₂)
4. Three gas wash bottles, Quickfit Dreschel borosilicate glass, 250 ml.
5. A circulator oil bath Thermo Scientific Haake, DL30-W15/B.

6. A glass reactor purchased from Fisher Scientific consisting of:
 - Vessel SLV reactor cylindrical borosilicate glass 1 L (product no SLV-110-110Y)
 - Lid SLV multipoint (product no SLV-110-050A)
 - Ring SLV sealing (product no SLV-110-230V)
 - Collar SLV for 100 mm flange (product no SLV-110-250P)
7. Gas distribution frit Pyrex with pore size 1, 14mm dia - Fisher Scientific (item number TUL-410-020A)
8. A coil condenser, Pyrex glass 207 mm length and cone 40/38

2.3.2 *Thermal Degradation Rig - Pressure vessels*

These vessels and associated equipment were designed in order to thermally degrade samples of different solvents quickly, meaning that it was necessary to operate at high temperatures and thus high pressures. The whole system consists of:

1. Three 0.6 L high pressure vessels with maximum working pressure of 20 MPa (2950 psi) and temperature range from -10 to 350 °C (product no 453HC3) all equipped with a rupture disk in case the pressure in the vessel exceeds 2000 psi (product no 526HCPF) purchased from Parr Instrument Company Ltd in the USA.
2. A needle pressure gauge 0-2000 psi (0 to 13.6 MPa) purchased from Parr Instrument Company Ltd (product no 593HCPF)
3. A digital pressure gauge purchased from OMEGA Ltd with the following specifications:
 - a. a pressure transducer with accuracy 0.08% and range 2500.0 psig (17 MPag)
 - b. a 0-15.0 V voltage logger
 - c. a USB interface cable/SW
 - d. OMEGASOFT for OM-CP series data logging software, version 2.02.5
4. A fan-assisted oven (Binder, see Figure 2.3) capable of maintaining temperatures up to 300 °C +/- 1 °C.

2.4 Experimental Methods

2.4.1 Determination of the effect of thermal degradation on CO₂ absorption and desorption

Unless otherwise stated the procedure was as follows.

A volume of 1200 ml of 30% wt aqueous MEA solution was contacted with pure CO₂ at a rate of 100 ml/min in the gas absorption/stripping rig (Figure 2.1), until the desired loading was achieved, as determined by TOC measurement. The resulting sample was put into the three high pressure vessels (Figure 2.3), 400 ml in each, and then the vessels were placed in the oven to be thermally degraded at 160°C. The pressure changes in two of the three vessels were continuously monitored, for safety reasons. The vessels were removed from the oven at predetermined times up to 8 weeks. Repeated absorption/stripping cycles were applied to samples of pure MEA in

the absorption/stripping apparatus (Figure 2.1) in order to determine the pure solvent's behaviour and its capacity for CO₂ uptake for a given period of time (approximately 6.5 hours for absorption and the same for stripping). For the absorption the temperature in the oil bath was raised to 50 °C and the feed gas inlet valve opened. 100 ml/min of pure CO₂ were bubbled into the reactor through a pre-saturator to maintain the water balance in the system. Any excess CO₂ gas that was not absorbed by the solvent was vented to a fume cupboard through a condenser and an amine recovery bottle. In order to determine the loading, samples of 0.1 ml were taken every 30 min and measured for their inorganic carbon content. After the absorption had finished the feed gas valve was closed. For the stripping the temperature in the oil bath was raised to 120 °C, the feed gas inlet valve opened and 200 ml/min of pure N₂ were bubbled into the reactor to ensure good agitation for efficient release of the CO₂ to the fume cupboard through the condenser and amine recovery bottle. The outlet gas flow and composition were measured every 20 to 30 min with a flow meter and microGC system. Repeated absorption/stripping cycles were then applied to the degraded samples so as to determine how thermal degradation affects the solvent's CO₂ uptake capacity. During the absorption the CO₂ loading of the sample was determined by measuring the carbon content of the sample with the TOC analyser. During stripping the microGC system was used to determine the CO₂ concentration at the outlet of the absorption/stripping rig. The samples were analysed for thermal degradation products with the GC-MS.

2.4.2 Analytical procedures

A considerable period of time in this project was spent on development of analytical procedures for both the ion chromatography and the gas chromatography, because of their key roles in delivering the initial project objectives. Exact details of the development processes have been omitted for clarity and only the final versions of the analytical techniques will be detailed herein.

2.4.2.1 Ion Chromatography (IC)

After extensive experimentation, mostly in collaboration with Dionex specialists in the UK and Switzerland, it was resolved to deactivate the MEA and its effect on the IC chromatographs and for that reason the Dionex On Guard II H cartridges (2.5 cc) were purchased in order to pre-process all the samples. This has the effect of removing the large diffuse peaks that were present at low residence times on the IC chromatographs by selectively sorbing the MEA onto the solid resins in the column whilst leaving the anions of interest unaffected. The cartridge tube was fitted to the bottom of a 25 ml syringe. In order to clean the cartridge 15 ml of DI water, at a flowrate of approximately 2 ml/min, were passed through the cartridge and discarded. Then, 10 ml of the aqueous MEA solutions were passed through the cartridge, the first 5 ml were discarded and the rest of the sample was analysed in the IC using the following conditions:

- eluent - potassium hydroxide, 30 mM,
- flow rate - 1.2 ml/min,
- temperature - 30 °C,
- injection volume - 10 µl

- suppressor current - 100 mA.

2.4.2.2 Gas chromatography – mass spectrometry (GC-MS)

Aqueous samples cannot be introduced to the GC-MS with the current set up, so the first step was to partition the organics from the water samples into diethyl ether. 50 ml of the sample were mixed in a volumetric flask with 50 ml of diethyl ether and shaken on a rotating bed for 2 days. 2 ml of the ether with the dissolved organics were then introduced to the GC-MS and run under the following conditions:

- GC

Experimental time 14.50 min

Split is 50 ml/min

Initial temperature 50 °C hold for 0.5 min, rate 20 °C/min to 320 °C hold for 0.5min

- MS

Duration 17 min

Start mass 10 m/z

End mass 200 m/z

3 RESULTS AND DISCUSSION

3.1 Detection limits and calibration curves for the IC and GC-MS

Based on an extensive literature search (e.g. Bello et al. 2005, Davis et al. 2008, Sexton et al. 2006, Sexton et al. 2008, Stratizar et al. 2001, Strazisar et al. 2003, Supap et al. 2006) some of the most common MEA degradation products (Table 3.1) were purchased. Experiments were performed to check if it was possible to detect them in aqueous MEA solutions using the GC-MS and IC, and to determine the lower detection limits.

Table 3.1 The most common oxidative and thermal MEA degradation products reported in the literature

State	Compounds
Oxidative	Formates (IC)
	Acetates (IC)
	Oxalates (IC)
	Nitrite / Nitrate (IC)
	HEI [Hydroxyethyl-formamide] *
	HEF [Hydroxyethylimidazole] *
Thermal	Ammonia
	HEEDA [N-(2-hydroxyethyl)-ethylenediamine] (GC-MS)
	MEA urea [N,N-di(2-hydroxyethyl)urea] *
	HEIA [1-(2-hydroxyethyl)-2-imidazolidinone] (GC-MS)
	2-Oxazolidone(GC-MS)

* Not purchased

In Table 3.2 the retention times determined for the major oxidative degradation products when analysed with the available IC system can be seen.

Table 3.2 Retention times in the IC system for the major oxidative degradation products

Analyte	Retention time (min)
Acetate	2.52
Formate	2.62
Oxalate	4.40
Nitrite	3.50
Nitrate	5.20
Sulfate	4.30

In Figure 3.1 an example of the calibration curves (oxalate ion) can be seen. All the calibration curves produced from the IC system were linear over the concentration range examined.

Table 3.3 shows the method detection limits (MDL, equal to three times the Standard Deviation obtained when analyzing blank solutions) for all the inorganic ions analysed in the available system using the method described in Section 2.4.2, Analytical Procedures.

Table 3.3 Method detection limits for anions in the IC

Analyte	MDL(mg/L)
Acetate	0.6
Formate	0.7
Oxalate	0.9
Nitrite	0.4
Nitrate	0.7

For MEA and its thermal degradation products, analyses were performed with the GC-MS and Figure 3.2 shows a clear peak response obtained for MEA when analysed using the method developed during this research project and described in Section 2.4.2. In Table 3.3 the retention times for MEA, HEEDA, HEIA and 2-Oxazolidone when analysed with the available GC-MS system can be seen.

Table 3.4 Retention time of each analyte for the available GC-MS system

Analyte	Retention Time (min)
MEA	3.31
HEEDA	6.72
HEIA	10.31
2-Oxazolidone	7.79

Figure 3.3 shows the calibration curve produced for MEA in diethyl ether. All the calibration curves produced by the method developed for MEA, HEEDA, HEIA and 2-oxazolidone in the ether were linear over the concentration ranges studied.

It can be concluded, with the systems and methods developed throughout this project, that the identification and quantification of MEA and its major oxidative and thermal degradation products is feasible.

3.2 Initial degradation experiments

A series of early experiments was performed with oxygen concentrations in the feed gas at more than three times the expected levels in practice to explore the rate of MEA degradation. A sample of 500 ml of 5 molal aqueous MEA solution was prepared and subjected to repeated cycles of absorption and stripping in the gas absorption/stripping rig (Figure 2.1). The feed gas was 20 ml/min CO₂ and 180 ml/min air, thus giving 66.4% N₂, 17.7% O₂ and 15.9% CO₂ on a weight basis. Each

absorption cycle lasted 2 hours and stripping 1 hour. The system was run for 14 full (absorption/stripping) cycles. The microGC system was used in order to measure the outlet gas composition, during both absorption and stripping, sampling every 10 minutes for all the periods of absorption and stripping.

In Figures 3.4 and 3.5 the microGC responses for all the 14 cycles of absorption and stripping respectively, are shown. It is observed that the absorption curves do not have any clear trend. The stripping curves are essentially identical within experimental error and demonstrate that the CO₂ concentration is essentially constant in less than one hour. These results show that in the presence of O₂ the 14 absorption/stripping cycles did not have any measurable effect on the MEA. Therefore, it was concluded that many more full cycles of absorption/stripping would need to be applied to the MEA, or higher pressures and O₂ concentrations introduced in order to observing any significant degradation.

This sample was also analysed for degradation products both in the GC-MS and the IC. For the GC-MS analysis at that stage of the project and method development, the organic compounds from the water sample were partitioned into dichloromethane (DCM) and the GC conditions were:

- Experimental time 17.83 min
- Split 20 ml/min
- Initial temperature 50 °C, hold for 0.50 min
- Final temperature 280 °C, hold for 2 min
- Rate 15 °C/min.

It was observed that HEIA, HEEDA and 2-oxazolidone were not present in this solution. It was concluded that either there were no thermal degradation products generated in the system after 14 full cycles or they were present at lower concentrations than the lower detection limit of the method and the GC-MS setup used. As mentioned in Section 2.4.2, a modified procedure was developed at a later stage of the project.

The IC chromatograph presented in Figure 3.6 shows that there are 3 peaks present which, based on the retention times, were used to identify nitrite, nitrate and sulfate ions. Two of the peaks were quantified and the presence of 111 mg/L nitrates and 1350mg/L nitrites determined. No calibration curve was made to determine the sulfate ion concentration. The same sample was then analysed with the HACH portable colorimeter and 560 mg/L nitrites, 29.6 mg/L nitrates and 6 mg/L sulfates were measured. It should be noted here that sulfate ions were not expected to be found in the samples. Clearly, there are differences between the absolute values of concentrations found by the two instruments but the trends are similar. Reconciliation of these differences in absolute concentrations would require further analytical investigation work.

At this stage of the project it was realised that it would not have been possible to degrade samples within a reasonable timescale and it was decided to focus the project on the thermal degradation of MEA and on how to accelerate the generation of thermally degraded samples. For this reason a new set of experiments was designed.

3.3 Thermal degradation

After it was realised that it would not be possible to degrade samples of MEA in the absorption/stripping rig, it was decided to take a more focused approach to thermal degradation.

3.3.1 CO₂ solubility in aqueous MEA solutions

There have been several studies of MEA degradation at temperatures up to 150°C. For this study it was decided to increase the temperature range in order to achieve faster degradation and also generate sufficient volumes of degraded samples to test in the absorption/stripping apparatus. This approach required operation at elevated pressures and the first step was to perform an extended literature review in order to have an idea of what pressures should be expected, primarily for safety reasons. Table 3.5 shows CO₂ partial pressures reported in the literature for 30% wt aqueous MEA solutions with different CO₂ molar loadings.

Table 3.5 CO₂ partial pressures reported in the literature for MEA solutions in water at loadings up to 1mole CO₂/mole MEA

Author	Temperature (°C)	CO ₂ Partial Pressure (kPa)
Mason and Dodge (1936)	0, 25, 50, 75	1.387-100.2
Lyudkovskaya and Leibush (1949)	25, 50, 75	255.3-4124
Goldman and Leibush (1959)	75, 100, 120, 140	0.5333-472.9
Lawson and Garst (1976)	94	23-453
Lee et al (1976)	25 - 120	0.2 - 6616
Nasir and Mather (1977)	100	0.0005-0.52
Shen et al (1992)	40, 60, 80,100	200-2000
Jou et al (1994)	0-120	100- 20000
Jou et al (1995)	0-150	0.001-20000
Ma'mum et al (2005)	120	7 - 192

It was concluded that despite an abundance of data, there is not clear consistency and values are to some extent dependant on their method of determination. It was, therefore, decided to repeat some of the experimental work and to generate new data appropriate to the rig in use for the present study. To this end a 400 ml sample of 30 % wt aqueous MEA solution was sealed in the high pressure vessels at 100 °C to determine the CO₂ partial pressure developed in the headspace as a function of loading. For that purpose solutions with different CO₂ molar loadings were prepared in the absorption/stripping rig, the loading being determined by measuring the inorganic carbon content in the samples with the TOC instrument. In the TOC instrument the sample was introduced into a solution of phosphoric acid which reverses the reaction of CO₂ with the MEA and releases all the CO₂ as a gas (Bishnoi & Rochelle 2000) which is then detected by a Nondispersive Infrared (NDIR) sensor. The samples were put in the high pressure vessels and placed in the forced convection oven at 100 °C. After the system reached equilibrium, in other words when the pressure remained stable for more than 1 hour, the pressure reading, shown on the needle pressure gauge, was taken. Figure 3.7 shows the time to equilibrium of the 400 ml of 30 % wt aqueous MEA solution with the CO₂ released into the headspace of the pressure vessel versus the initial CO₂ molar loading of the

MEA solution at 100 °C. It should be noted that these experiments were very time consuming to perform and hence the limited data set.

The CO₂ partial pressure was calculated by subtracting from the total pressure the partial pressures of MEA, H₂O (both calculated using Raoult's law) and the air partial pressure (calculated assuming ideal gas behaviour). In Figure 3.8 the graphic representation of the CO₂ partial pressure versus CO₂ molar loading is shown.

At this stage, and after comparing the CO₂ solubility data produced for 100°C with the values found in the literature, some iterative calculations were performed for 160°C. It was concluded that it was safe to place the high pressure vessels in the oven at 160°C for up to 8 weeks, because the calculated pressure was within the operating limits of the pressure vessels purchased. The “worse case scenario” of complete degradation of the MEA and release of all the available CO₂ into the headspace was used.

3.3.2 Degradation experiment – “lean” initial molar loading

3.3.2.1 Procedure

In order to degrade samples in a reasonable timescale, the temperature of 160°C was chosen for the experiments. According to Davies & Rochelle (2008) and Lepaumier et al. (2009 & 2010) the MEA degradation products are the same at 100, 120, 135, 140 and 150°C, it is only the rate of their production that increases with the temperature.

For the degradation experiment, three 400 ml samples of 30 % wt aqueous MEA solutions were loaded in the absorption/stripping rig (Figure 2.1) with initial molar loading of 0.19 (moles of CO₂/mole of MEA) as determined by the TOC. The samples were sealed in the high pressure vessels (Figure 2.3) and placed in the oven at 160 °C. The pressure change inside one of the vessels was continuously monitored with an analogue pressure gauge for safety reasons; it was assumed – as the experimental conditions were the same – that the pressure changes were the same in all the three vessels. The vessel equipped with the pressure gauge came last out of the oven. The samples were left in the oven at 160 °C for 2, 3 and 8 weeks to thermally degrade. Each one of the samples was taken out of the oven and remained sealed at room temperature until the beginning of the absorption/stripping experiment.

The total pressure change throughout a typical experiment is shown in Figure 3.9. The pressure profile is not as originally expected. It was thought that as the MEA degraded the CO₂ that was bound to the MEA would have been released into the headspace causing the total pressure in the vessel to increase. In practice, after the initial expected rapid increase, the pressure started dropping almost immediately and it kept dropping for 420 hours. This could be explained by the fact that MEA reacts with CO₂ in order to degrade which can be seen in the schematic representation of the thermal degradation products proposed by Davies, 2009 (see Figure 3.10). It could also mean that at those pressures developed in the vessel's headspace part of the CO₂ that was initially released by the MEA solution is reabsorbed. It could also mean that there was a leak in the vessel.

Each of the three samples was taken out of the high pressure vessels and its volume was measured at room temperature using the same volumetric tube used to measure the initial sample volumes (400 ml). Table 3.6 presents the volumes of all the three degraded samples.

The initial volume of the samples was 400 ml and as can be seen in Table 3.6 there was no considerable change in the volumes after the degradation experiment. This is not absolute proof that no leakage of CO₂ had occurred but it must be noted that when the vessels did leak during other studies there were visible signs and a considerable loss of liquid content. It is interesting to note that other workers (eg Lepaumier et al, 2010) have made similar observations and discussed them in an almost identical manner.

Table 3.6 Volumes of the three degraded samples after the end of the “lean” degradation experiments

Sample	Volume (ml)
2 weeks	396
3 weeks	398
8 weeks	397

All the samples were then tested and compared against a pure MEA sample of the same initial concentration (30 % wt) to determine how the thermal degradation affected the solvent’s CO₂ uptake capacity.

3.3.2.2 *Effect of degradation on the ability of the solvent to absorb and release CO₂*

After the end of the degradation experiment all the samples were tested in the absorption/stripping rig. The first step was to release the CO₂ left in the solutions by performing stripping. The microGC was used to determine the CO₂ volume released by the samples. The exit flow and the outlet gas composition were measured every 20 minutes. The volume of CO₂ was then calculated by multiplying the CO₂ percentage with the exit flow rate and the time (20 minutes). A flow correction was applied as during the stripping the exit flow meter is calibrated for nitrogen but a mixture of CO₂ and N₂ was exiting the system. In Figure 3.11 the cumulative CO₂ volume released by the degraded samples can be seen. It is observed that the longer the sample remained in the oven the less CO₂ it releases during the subsequent stripping stage. This is again consistent with the expectation that formation of degradation products requires CO₂. Table 3.7 shows the volumes of CO₂ released by all the three degraded samples with initial concentration of 30% wt aqueous MEA and initial molar loading of 0.19 after being kept at 160°C for the allocated times of 2, 3 and 8 weeks.

Table 3.7 Volume of CO₂ released during 1st stripping following degradation

Sample	CO ₂ volume released (L)	Experimental Time (min)
2 weeks	3.4	380
3 weeks	2.3	180
8 weeks	0.9	400

Note: Initial concentration 30% wt aqueous MEA solution, 0.19 initial molar loading, degradation temperature 160 °C

It should be noted here that the samples were initially loaded with 8.3 L of CO₂ and that CO₂ evolution was still happening when stripping was stopped for the 2-week and 3-week samples. What is clear is that the sample held in the oven for 8 weeks has “lost” 7.4 litres of CO₂.

After the first stripping the samples were cooled down and the next day were loaded with CO₂ in the absorption/stripping rig. For the absorption the temperature in the oil bath is raised to 50 °C and it takes up to 10 minutes for this temperature to be reached. At that point the inlet gas feed valve was opened and pure CO₂ was bubbled into the reactor at a flow rate of 100 ml/min. The amount of CO₂ captured by the MEA was determined by measuring the inorganic carbon content of the solution using the TOC instrument. Originally, the microGC was also used to determine the amount of CO₂ that is absorbed by the MEA but this method was subsequently shown to be inaccurate. Figure 3.12 shows the graphical representation of the volume of CO₂ captured by the degraded samples over time for all three samples.

From Figure 3.12 it can be observed that the 8-week sample stops absorbing CO₂ after approximately 1 hour of bubbling and it absorbs about 4.9 L of CO₂. The samples after 2 and 3 weeks of thermal treatment seem to stop absorbing at almost the same time (after about 300 minutes). At this point it is important to consider the volumes of CO₂ that remained in the degraded samples after the first stripping. These were determined by TOC and were 2.7 L, 0.9 L and 0.9 L for the 2, 3 and 8 week degraded samples respectively.

A pure MEA solution with 30% wt initial concentration has the potential to absorb about 23 L of CO₂ and on this basis it is concluded that the “lean” solution after 8 weeks of thermal degradation has lost approximately 75% of its ability to absorb the gas i.e. 5.8 L of gas absorbed compared to a theoretical capacity of 23 L. According to Davies (2009) a 7 molal (30% wt) aqueous MEA solution with initial molar loading of 0.20 after degrading for 8 weeks at 135 °C has an approximately 29% MEA loss.

After the end of the absorption, stripping was performed again in the normal manner. In Figure 3.13 the cumulative CO₂ released from the three degraded samples can be seen. The resulting curves are compared with the one produced for a 400 ml fresh 30% wt aqueous MEA sample. Table 3.8 summarises the absorption and stripping results for the samples with “lean” loading after being subjected to the thermal degradation process.

Table 3.8 Absorption/Stripping behaviour of thermally degraded, lean-loaded MEA samples after removal of residual CO₂

Sample and degradation time	Volume of CO ₂ absorbed in 400 min (L)	Volume of CO ₂ stripped in 400 min (L)
Pure MEA (no thermal treatment)	9.9*	9.9
Lean-loaded 2 weeks	8.8	8.7
Lean-loaded 3 weeks	7.8	7.3
Lean-loaded 8 weeks	5.8	3.7

* Inferred – not measured

In Table 3.8 it can be observed that there is a tendency for the CO₂ to be retained in solution during the stripping stage and that this trend is more prominent for the 8-week sample. However it is recalled that the absorption data were obtained by TOC measurements and the stripping by microGC, hence further cycles of absorption and stripping are necessary to explore this phenomenon in more detail.

3.3.2.3 Determination of concentrations of degradation products in solution

After the end of the tests to assess how degradation affects the solvent's CO₂ uptake and stripping capacity, the degraded samples were analysed in the GC-MS to identify and quantify any thermal degradation products generated. In addition to this the concentration of the MEA left in solution was also determined. Figures 3.14, 3.15 & 3.16 show the peak responses produced by the GC-MS when the samples that degraded for 2, 3 and 8 weeks were analysed. In Table 3.9 all of the compounds present in the 3 samples, as determined by the GC-MS analysis software, have been listed. The ones in bold have been previously reported in the literature as MEA degradation products (Stratizisar B. R. et al. 2002, Stratizisar B. R. et al. 2003, Supap T. et al. 2006, Davies PhD thesis 2009, Lawal O. et al. 2005, Bello A. et al. 2005).

Table 3.9 Degradation products found in the “lean” degraded samples

Degradation Product	Week 2	Week 3	Week 8
HEEDA	+	+	+
HEIA	+	+	+
2-oxazolidone	+	+	
1,2-ethanediol	+		+
1-amino-2-propanol			+
piperazine	+	+	+
1-(2-aminoethyl)imidazole			+
2-methylpiperazine			+
2,5-dimethylpiperazine			+
2-methyl-3-oxazolidine		+	+
4-methylmorpholine			+
4-morpholineethanol	+	+	
diisopropanolamine	+		+
2-imidazolidinone	+		+
3-methyl-oxazolidone	+	+	
Tris(2-aminoethyl)amine			+
1-piperazineethanol			+
1,3-propanediamine			+
1,4-bis(2-hydroxyethyl)piperazine	+	+	+
N,N'-bis(2-aminoethyl)-1,2-ethanediamine	+	+	+
1-(2-(2-hydroxyethoxy)ethyl)piperazine	+	+	+
3-(2-hydroxyethyl)-2-oxazolidinone	+	+	+

Note: Initial concentration 30% wt aqueous MEA solution, initial molar loading of 0.19, degradation temperature 160°C

It is interesting to note that this study has identified piperazine and other related compounds in all three of the degraded samples. Full quantification was not

possible during the project but a preliminary determination of piperazine alone gave a concentration lower than 0.2% w/v.

After the compounds found in solution were identified, a detailed programme of work to quantify MEA, HEEDA, HEIA and 2-oxazolidone concentrations in the degraded solvents was performed. It was noted very early in this work that not all of the analytes were recovered by the liquid/liquid extraction process and it was necessary to quantify their partitioning into the diethyl ether. Solutions containing a known concentration of each compound were prepared and the liquid/liquid extractions performed. The resulting solutions of the compounds in the diethyl ether were then measured by the GC-MS and the concentration determined from the calibration curve detailed in Section 3.1. The ratio of this concentration to the known concentration is termed the Partition Coefficient in the present work. Values of these coefficients expressed as a percentage for MEA, 2-oxazolidone and HEEDA are presented in Table 3.10. It was not possible to obtain consistent values for HEIA despite considerable investigation and for that reason an alternative approach involving determination of a calibration curve directly from known aqueous solutions after extraction into the ether was developed. It was estimated that the accuracy of these analytical procedures is not better than +/- 15%.

Table 3.10 Partition coefficients for MEA, HEEDA and 2-oxazolidone into diethyl ether

Analyte	Partition Coefficient %
MEA	9
HEEDA	20
2-oxazolidone	100

Table 3.11 shows the concentration of MEA, HEIA, 2-oxazolidone and HEEDA in the three degraded samples with the “lean” initial loading (0.19 moles of CO₂ / mole of MEA).

Table 3.11 MEA and its major thermal degradation products concentrations—“lean” samples

Compound	Sample		
	2 weeks (% v/v)	3 weeks (% v/v)	8 weeks (% v/v)
MEA	12.8	8.7	1.2
HEIA	0.3	3.2	11.9
HEEDA	0.3	0.3	0.9
2-Oxazolidone*	1.6	0.9	-

Initial concentration 30% wt (or 29.6 % v/v) aqueous MEA solution, 0.19 initial molar loading, degradation temperature 160°C

*The 2-oxazolidone concentrations are in % w/v

These data show that as the degradation experiment progresses, the MEA concentration decreases steadily from almost 30% v/v to about 1% v/v. The 2-oxazolidone appears during the first two weeks and is then reduced over time, whereas HEEDA is almost stable for the first 3 weeks and then it slightly increases. According to Davies (2009) the first degradation product produced from MEA is 2-

oxazolidone (see Figure 3.10). Lepaumier et al. (2009) suggests that oxazolidones react very easily with another amine to give addition products. Therefore, the absence of 2-oxazolidone from the 8 weeks sample is what would be expected from these previous studies. HEIA concentrations grew as the degradation time increases and it is the major product in the 8-week sample.

3.3.2.4 Corrosion

After the end of the degradation experiment and when the pressure vessels were opened, it was noted that quite noticeable volumes of solids were present in all the 3 degraded samples. At that point after an inspection of the pressure vessels, corrosion was suspected. For that reason after the absorption/stripping experiment, all the three samples were filtered (Whatman, 90 mm dia, catalogue number 1440090) in order to be analysed for metals by ICP (Section 2.2). As the masses of solids in solution were not enough for the ICP analysis (at least 0.10 g of dried solids needed) for the 2 and 3 week samples, only the solids from the 8-week sample were analysed along with all of the liquid samples. The results can be seen in Table 3.12 for the solid sample and Table 3.13 for the liquid samples.

Table 3.12 Analysis of metal content of the solids in the aqueous MEA sample that degraded for 8 weeks

Sample	Cr (g/kg)	Fe (g/kg)	Mn (g/kg)	Mo (g/kg)	Ni (g/kg)
8 weeks	112.5	722	0.5	4.3	2.4

Note: Sample of 0.101 g of dried solids filtered from the 400 ml of 30% wt aqueous MEA solution with initial CO₂ molar loading of 0.19 after degrading for 8 weeks at 160 °C in the pressure vessels.

Table 3.13 Analysis of metal content of the three degraded samples of MEA compared with a sample of fresh MEA.

Sample	Cr (mg/L)	Fe (mg/L)	Mn (mg/L)	Mo (mg/L)	Ni (mg/L)
Fresh MEA	0	0	0	0.1	0
2 Weeks	16.6	19.7	0	20.0	149.3
3 Weeks	16.5	27.3	0	24.3	224.7
8 Weeks	20.4	366.2	0.4	67.6	929.2

Note: 400 ml 30% wt aqueous MEA solutions with initial CO₂ molar loading of 0.19 degraded for 2, 3 and 8 weeks at 160 °C compared with a 30% wt aqueous fresh MEA, volume of the analysed sample 2 ml.

The metal losses per unit area and per unit area over time of the degradation experiments were determined, taking the vessel's surface area as 282.6 cm² and the time as the degradation experiment duration. The results are presented in Table 3.14.

Table 3.14 Corrosion rates of the high pressure vessels during the degradation experiments of MEA with “lean” initial molar loading

	mg Cr/cm ²	mg Cr/cm ² /day
2 weeks	0.023	0.002
3 weeks	0.024	0.001
8 weeks	0.029	0.0005
	mg Fe/cm ²	mg Fe/cm ² /day
2 weeks	0.028	0.002
3 weeks	0.039	0.0018
8 weeks	0.518	0.0093
	mg Mo/cm ²	mg Mo/cm ² /day
2 weeks	0.028	0.002
3 weeks	0.034	0.0016
8 weeks	0.096	0.0017
	mg Ni/cm ²	mg Ni/cm ² /day
2 weeks	0.211	0.015
3 weeks	0.318	0.0151
8 weeks	1.315	0.024

Kongstein and Schmid (2010) determined the corrosion rate and corrosion potential for bare 316 L Steel in 5 M MEA solution at 135 °C with 10 % CO₂. The corrosion rate starts at 0.35 mm/y and drops to 0.15 after 50 hours of experiment. Based on metal content in solution determined in the 8weeks liquid sample (see Table 3.13) it is calculated that the overall corrosion rate in the present work is 1.95 mm/y, a value somewhat higher than theirs. This could be in part due to the operating temperature and also to differences in the stainless steels used in the studies.

3.3.3 Degradation experiment – “rich” initial molar loading

3.3.3.1 Procedure

Three 400 ml samples of 30 % wt aqueous MEA solutions were loaded in the absorption/stripping rig to an initial molar loading of 0.37 as determined by inorganic carbon content measurement. The pressure change inside two of the vessels was continuously monitored with an analogue pressure gauge (3-weeks sample vessel) and a digital gauge (8-weeks sample vessel) for safety reasons. The total pressure changes throughout the experiment are shown in Figure 3.17. The final pressure readings of both the gauges were quite close to each other, but it is interesting to note that the needle pressure gauge shows an initial rapid increase then a slight decrease in pressure until they converge after approximately 200 hours. This trend is similar, but of smaller magnitude, to that noted for the “lean” sample (see Figure 3.9).

The samples were left in the oven sealed at 160 °C for 2, 3 and 8 weeks to thermally degrade. Each one of the samples was taken out of the oven and remained sealed at room temperature until the beginning of the absorption/stripping experiment.

After the end of the degradation experiment, each of the three samples was taken out of the high pressure vessels and its volume was measured at room temperature using the same volumetric tube used to measure the initial sample

volumes (400 ml), The volumes were almost identical and showed little change compared to the initial values (see Table 3.15).

Table 3.15 Volumes of the three degraded samples after the end of the degradation experiments

Sample	Volume (ml)
2 weeks	396
3 weeks	399
8 weeks	401

Note: Initial volume 400 ml, initial concentration 30% wt aqueous MEA solution, 0.37 initial molar loading, degradation temperature 160 °C

3.3.3.2 Effect of degradation on the ability of the solvent to absorb and release CO₂

The first step was to remove the CO₂ left in the solutions and the microGC was used to determine the volume released by the samples. The CO₂ volume was calculated in the same way as described for the “lean” sample and in Figure 3.18 the cumulative CO₂ volume released by the degraded samples can be seen. Once again it was observed that the longer the thermal treatment the less CO₂ was released. In this case the pressure reduction in the vessels was very small and little if any CO₂ could have been lost by leakage. The loss of CO₂ must, therefore correspond to its uptake in forming the degradation products. Table 3.16 shows the volumes of CO₂ released by the three degraded samples with initial concentration of 30% wt aqueous MEA and initial “rich” molar loading of 0.37 after treatment at 160°C. It should be noted here that the samples were initially loaded with 16.1 L of CO₂.

Table 3.16 Volume of CO₂ released during 1st stripping of the degraded “rich” samples

Sample	CO ₂ volume (L)
2 weeks	9.1
3 weeks	6.3
8 weeks	2.4

Note: Initial concentration 30% wt aqueous MEA solution, 0.37 initial molar loading, degradation temperature 160 °C

After the first stripping the samples were loaded with CO₂ in the absorption/stripping rig, the procedures followed both during the experiment and the results processing were the same as described for the “lean” degraded samples. Figure 3.19 shows the graphical representation of the volume of CO₂ captured by the degraded samples over time for all the three degraded samples. The sample after 8 weeks of degradation (Rich 8) stops absorbing after about 50 minutes whereas the samples of 2 and 3 weeks duration continue absorbing for almost 150 min. Once again

it is important to consider the volumes of CO₂ that remained in the degraded samples after the first stripping. These were determined by TOC and were 2.3 L, 1.1 L and 0.9 L for the 2, 3 and 8 weeks degraded samples respectively. As expected, Rich 8 absorbs less CO₂ than the other two, whereas the sample after 2 weeks of thermal treatment absorbs the most CO₂ (see Table 3.17). Recalling that about 23 L of CO₂ could potentially be absorbed it is estimated that the “rich” solution after 8 weeks of thermal degradation has lost approximately 78 % of its ability to absorb the gas, a value slightly in excess of that found for the “lean” case.

After the end of the absorption, stripping was performed in the normal manner. In Figure 3.20 the cumulative CO₂ released from the three degraded samples when compared with a pure MEA sample of the same initial concentration can be seen. It is observed that the samples of 2 and 3 weeks degradation stop releasing CO₂ almost at the same time, but the sample of 2 weeks releases a little more (see Table 3.17). The 8 weeks sample releases considerably less CO₂ than the other two.

Table 3.17 Absorption/Stripping behaviour of thermally degraded, rich-loaded MEA samples after removal of residual CO₂

Sample and degradation time	Volume of CO ₂ absorbed in 400 min (L)	Volume of CO ₂ stripped in 400 min (L)
Pure MEA (no thermal treatment)	9.9*	9.9
Rich-loaded 2 weeks	8.6	8.1
Rich-loaded 3 weeks	7.6	7.4
Rich-loaded 8 weeks	5.1	4.0

* *Inferred – not measured*

It is interesting to note that like the “lean” sample (Table 3.8) there is evidence of retention of CO₂ after absorption, suggesting a different mechanism than for pure MEA. More work is required to confirm this observation.

3.3.3.3 Determination of concentrations of degradation products in solution

After the end of the test to assess how degradation affects the solvent’s CO₂ uptake capacity, the degraded samples were analysed in the GC-MS to identify and quantify any thermal degradation products generated. In addition to this the concentration of the MEA left in solution was also determined. Figures 3.21, 3.22 & 3.23 show the peak responses produced by the GC-MS when the samples that were degraded for 2, 3 and 8 weeks were analysed respectively. In Table 3.18 all of the compounds detected by the GC-MS software in the 3 samples are listed. The ones in bold have been previously reported in the literature as MEA degradation products (Stratizisar et al. 2002, Stratizisar et al. 2003, Supap et al. 2006, Davies, PhD thesis 2009, Lawal et al. 2005, Bello et al. 2005)

As for the “lean” sample it is again interesting to note that this study has identified piperazine and other related compounds in all three of the degraded samples. Full quantification was not feasible during the project but a preliminary determination of piperazine alone gave concentration lower than the detection limit of 0.1% w/v. However, in view of the large molecular masses of some of these compounds, very small concentrations are sufficient to account for the carbon originally present in the MEA.

Table 3.19 shows the concentration of MEA, HEIA, 2-oxazolidone and HEEDA determined in the three degraded samples with the “rich” initial loading (0.37 moles of CO₂ / mole of MEA).

Table 3.18 Degradation products found in the degraded samples with initial “rich” loading

Degradation Product	Week 2	Week 3	Week 8
HEEDA	+	+	+
HEIA	+	+	+
2-oxazolidone	+	+	+
1,2-ethanediol		+	+
1-amino-2-propanol	+		
piperazine**	+	+	+
1-(2-aminoethyl)imidazole		+	+
2-methyl-3-oxazolidine	+		
4-methylmorpholine			+
diisopropanolamine			+
2-imidazolidinone	+	+	+
3-methyl-oxazolidone		+	+
1-piperazineethanol			+
1,3-propanediamine		+	+
1,4-bis(2-hydroxyethyl)piperazine	+	+	+
N,N'-bis(2-aminoethyl)-1,2-ethanediamine	+	+	+
1-(2-(2-hydroxyethoxy)ethyl)piperazine		+	+
3-(2-hydroxyethyl)-2-oxazolidinone		+	+

Initial concentration 30% wt aqueous MEA solution, initial molar loading of 0.37, degradation temperature 160°C

*** Present but at concentrations below instrument detection limits*

Table 3.19 MEA and its major thermal degradation products concentrations—“rich” samples

Compound	Sample		
	2 weeks (% v/v)	3 weeks (% v/v)	8 weeks (% v/v)
MEA	9.3	4.6	0.6
HEIA	2.0	4.5	17.0
HEEDA	1.1	1.1	2.2
2-Oxazolidone*	6.3	5.9	4.5

Note: initial concentration of 30% wt (or 2.6 % v/v) aqueous MEA solution and 0.37 initial molar loading

**The 2-oxazolidone concentrations are in % w/v*

The trends in this table are similar to those found for the “lean” sample and reported in Table 3.11. Of note are the very low final concentrations of MEA determined by the analysis procedure developed in the present work, showing degradations of the original amine in excess of 95% in 8 weeks at 160 °C. The absorption/stripping study suggested a somewhat lower degradation of the MEA as evidenced by the ability of the degraded solvents to remove CO₂ from the feed gas streams. However, this may be a reflection of the ability of some of the degradation products to absorb and release CO₂. Despite this difference both approaches demonstrate that there is very significant destruction of MEA at this temperature. However, it is worth reiterating that plant operation at this elevated value would not take place.

As previously mentioned, the quantification of every one of the identified products was not feasible in the present project. However, in order to add confidence to the stated analytical results a carbon balance was performed for each of the degraded samples. Whilst it is not possible in general to account for all of the C originally present in the MEA by the incomplete number of compounds that were quantified, this was possible in the 8 weeks degraded sample at “rich” loading. On this basis it is entirely feasible that the thermal degradation products; 2-oxazolidone, HEEDA and HEIA represent the vast majority of the species in solution after intense degradation.

3.4 Summary discussion and findings regarding solvent degradation

As demonstrated by the considerable numbers of publications in the field of CO₂ capture by amines listed in the Bibliography, there exists a large body of knowledge in this general area. Amine solvents for the uptake and subsequent release of CO₂ have been used for decades but very little research was performed on the detailed chemistries of the processes involved for many years until a resurgence of recent interest. For example the structure of the MEA-carbamate has been the focus of considerable attention during the last decade. However, there are very few recent papers of immediate relevance to the objectives of the present project. Furthermore these originate from fewer than six centres around the world where high quality research of this kind is currently being performed. Because of its practical relevance in flue gas applications, most of the information in the public domain is rightly concerned with oxidative degradation of amine solvents (eg Bello et al. 2005, Sexton et al. 2006, Sexton et al. 2008, Stratizar et al. 2001, Strazisar et al. 2003, Supap et al. 2006) and just a few (eg Davis et al. 2008) look at thermal degradation and the products of that process. With so few sources of data to examine it is not surprising that there is no overwhelming consensus on some of the important issues such as the extent of solvent deterioration and the quantities and qualities of the chemical products of degradation. The ability to quantify the chemistries of the various solutions generated during the research studies is key to extending fundamental understanding and yet again there are outstanding challenges concerning the analytical techniques to apply. The literature has examples of contradictory results for chemical speciation, including lack of universal agreement on the final stable products of thermal degradation of the most commonly used solvent, MEA. The most recent work (Davis, J. (2009) and Lepaumier, H., Picq, D. & Carrette, P. L. (2010))

agree that HEIA is the most stable of the species whilst a much earlier study by Polderman, L. D. & Dillon C.P. (1955) quote HEIA as being a precursor for HEEDA.

Considerable work has been done in the present study to optimise the techniques of GC-MS and ion chromatography in particular as tools to examine the mechanisms at work when MEA is exposed to chemicals other than CO₂ and to temperatures higher than those commonly found in operational plants. Despite this effort it has still not been possible to quantify all of the species of interest. However there are key findings that are listed here:

- the limited extent of oxidative degradation performed in this study showed little deterioration in solvent efficiency but the presence of relatively large amounts of anions such as nitrate and nitrite were found
- thermal degradation products reported in the literature have been found in solution and the major compounds identified. It has not been possible to identify any major environmental or health implications for these compounds from publically available data bases
- thermal degradation at 160 °C reduces the MEA content by as much as 95% as evidenced by absorption/stripping behaviour and chemical analysis
- there is conclusive evidence to show that despite the loss of almost all of the MEA by thermal degradation, the remaining solvent still has the ability to remove CO₂ but the sustainability of solvent efficiency with repeated cycles of adsorption/desorption is uncertain
- there is some evidence to support the rate of thermal degradation being enhanced as the amount of CO₂ in solution increases, but this effect is low at the elevated temperatures used in the present work
- the research work supports the findings that HEIA is probably the most stable thermal degradation product. This is based in part on the increasing amounts of this compound in the residual solvents after degradation and supported by calculations of the balance of C in solution for rich initial CO₂ loadings.

4 CONCLUSIONS

The major conclusions from the largely experimental study performed under this BCURA contract are listed as follows:

- the rig built to perform repeated absorption and desorption is now available to extend the work performed with MEA with varying gas properties and to include other solvents
- other equipment and procedures are available to perform accelerated solvent thermal degradation studies
- corrosion products were found in the solutions following thermal degradation and an overall corrosion rate of almost 2 mm per year was found at 160°C for the particular stainless steel vessels used
- procedures are now available to detect, identify and quantify the major MEA oxidative and thermal degradation products
- even at limited exposure of MEA to oxygen during repeated cycles of absorption/desorption, significant concentration of nitrites and nitrates were found
- thermal degradation at 160 °C for 8 weeks reduces the MEA content by as much as 95% as evidenced by absorption/stripping behaviour and chemical analysis
- despite the loss of almost all of the MEA by thermal degradation, the remaining solvent still has the ability to remove and release CO₂
- there is some evidence to support the rate of thermal degradation being enhanced as the amount of CO₂ in solution increases, but this effect is low at the elevated temperatures used in the present work
- a range of degradation products have been identified that correspond to those recently cited in the literature
- HEIA is shown to be the most stable thermal degradation product
- the major thermal degradation products are not associated with particular environmental or health effects.

5 BIBLIOGRAPHY – REFERENCES

- Abu-Zahra M.R.M, Schneiders L.H.J, Niederer J.P.M, Feron P.H.M, Versteeg G.F.**, 2007: “CO₂ capture from power plants Part I. A parametric study of the technical performance based on monoethanolamine”, *International journal of greenhouse gas control* I, pp 37 – 46.
- Abu-Zahra, M.R.M, Schneiders, L.H.J, Niederer, J.P.M, Feron, P.H.M, Versteeg, G.F.**, (2007) CO₂ capture from power plants Part I. A parametric study of the technical performance based on monoethanolamine, *International journal of greenhouse gas control*, 1, 37 – 46.
- Bai, H. & Yeh, A. C.** (1997) Removal of CO₂ Greenhouse Gas by Ammonia Scrubbing, *Ind. Eng. Chem. Res.*, 36, 2490-2493
- Bello, A. & Idem, R. O.** (2005) Pathways for the formation of products of the oxidative degradation of CO₂-loaded concentrated aqueous monoethanolamine solutions during CO₂ absorption from flue gases. *Industrial and Engineering Chemistry Research*, 44, 945-969.
- Bello, A. & Idem, R. O.** (2006) Comprehensive study of the kinetics of the oxidative degradation of CO₂ loaded and concentrated aqueous monoethanolamine (MEA) with and without sodium metavanadate during CO₂ absorption from flue gases, *Industrial and Engineering Chemistry Research*, 45, 2569-2579.
- Bishnoi, S. & Rochelle, G. T.** (2000) Absorption of Carbon Dioxide into Aqueous Piperazine: Reaction Kinetics, Mass Transfer and Solubility, *Chemical Engineering Science*, 55, 5531-5543
- Bishnoi, S. & Rochelle, G. T.** (2002) Absorption of Carbon Dioxide in Aqueous Piperazine/Methyldiethanolamine, *AIChE Journal*, 48, 2788-2799.
- Bishnoi, S. & Rochelle, G. T.** (2002) Thermodynamics of Piperazine/Methyldiethanolamine/ Water/ Carbon Dioxide, *Ind. Eng. Chem. Res.*, 41, 604-612.
- Blanchly, C. H. & Ravner, H.** (1966) Stabilization of Monoethanolamine Solutions in Carbon Dioxide Scrubbers, *Journal of Chemical and Engineering Data*, 11, 401-403.
- Bonenfant, D., Mimfault, M. & Hausler, R.** (2003) Determination of the Structural Features of Distinct Amines Important for the Absorption of CO₂ and Regeneration in Aqueous Solution. *Ind. Eng. Chem. Res.*, 42, 3179-3184.
- Chakma, A. & Meisen, A.** (1988) Identification of Methyl Diethanolamine Degradation Products by Gas Chromatography and Gas Chromatography and Chromatography-Mass Spectrometry”, *Journal of Chromatography*, 457, 287-297
- Chakma, A. & Kybett, B. D.** (2001) Kinetics of the oxidative degradation of aqueous monoethanolamine in a flue gas treating unit. *Industrial and Engineering Chemistry Research*, 40, 3445-3450.
- Chi, S. & Rochelle, G. T.** (2002) Oxidative degradation of monoethanolamine. *Industrial and Engineering Chemistry Research*, 41, 4178-4186.
- Cheng M.-D., Caparanga A. R., Soriano A. N. and M.-H. Li** (2009) Solubility of CO₂ in the Solvent System (water + monoethanolamine + triethanolamine), *J. Chem. Thermodyn.*

- Davis, J. & Rochelle, G. T.** (2008) Thermal degradation of Monoethanolamine at stripper conditions. *9th International Conference on Greenhouse Gas Control Technologies*, Washington DC.
- Davis, J.** (2009) Thermal degradation of Aqueous Amines Used for Carbon Dioxide Capture. *PhD thesis University of Texas at Austin*.
- Dawodu, O. F. & Meisen, A.** (1996) Degradation of alkanolamine blends by carbon dioxide. *Canadian Journal of Chemical Engineering*, 74, 960-966.
- Daubert, T. E., Jalowka, J. W. & Doren V.** (1987) Vapor pressure of 22 pure industrial chemicals. *AICHE SYMP. SERIES*, 256, 83, 128-156.
- Dodds, W. S., Stutzman, L. F. & Sollami, B. J.** (1956) Carbon dioxide solubility in water. *Industrial and Engineering Chemistry*, 1, 1, 92-95.
- Freguia, S., Rochelle, G. T.,** (2003) Modelling of CO₂ Capture by Aqueous Monoethanolamine”, *AICHE Journal*, 49, 7, 1676-1686
- Gardiner J. & Zabel T.** (1991) United Kingdom Water Quality Standards Arising from the European Community Directives.
- Goff, G. S. & Rochelle, G. T.** (2006) Oxidation inhibitors for copper and iron catalyzed degradation of monoethanolamine in CO₂ capture processes. *Industrial and Engineering Chemistry Research*, 45, 2513-2521
- Goldman, A. M. and Leibush, A. G.** (1959) Study of the Equilibrium of Carbon Dioxide Desorption from Monoethanolamine Solutions in the Temperature Range 75-140 °C. *Tr. Gos. Nauchno-Issled. Proektn. Inst. Azotn. Promsti.*, 10, 54-82
- Hagewiesche, D. P., Ashour, S. S., Al-Ghawas, H. A. and Sandall, O. C** (1995) Absorption of Carbon Dioxide into Aqueous Blends of Monoethanolamine and N-Methyldiethanolamine, *Chemical Engineering Science*, 50 (7), 1071-1079
- Heaton C.A.,** (1986) *The Chemical Industry*. 1st edition, Blackie & Son
- Hoffman R.V.** (2004) *Organic Chemistry*. 2nd edition, Wiley.
- Hook, R. J.** (1997) An Investigation of some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds, *Ind. Eng. Chem. Res.*, 36, 1779-1790
- Idem, R., Wilson, M., Tontiwachwuthikul, P., Chakma, A., Veawab, A., Aroonwilas, A. & Gelowitz, D.** (2006) Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology development plant and the boundary dam CO₂ capture demonstration plant. *Industrial and Engineering Chemistry Research*, 45, 2414-2420
- Jou, F.-Y., Otto, F. D. & Mather A. E.** (1994) Vapor-liquid equilibrium of carbon dioxide in aqueous mixtures of Monoethanolamine and methyldiethanolamine. *Ind. Eng. Chem. Res.*, 33, 2002-2005
- Jou, F.-Y., Mather A. E. & Otto, F. D.** (1995) The solubility of CO₂ in a 30 % mass percent Monoethanolamine solution. *The Canadian journal of chemical engineering*, 73, 140-147
- Kaewsichan, L., Al-Bofersen, O., Yesavage, V. F. & Selim M. S.** (2001) Predictions of the solubility of acid gases in Monoethanolamine (MEA) and methyldiethanolamine (MDEA) solutions using the electrolyte-UNIQUAC model. *Fluid Phase Equilibria*, 183-184, 159-171.
- Kapteina, S., Slowik, K., Verevski S. P. & Heitz A.** (2005) Vapor pressures and vaporization enthalpies of a series of ethanolamines. *J. Chem. Eng. Data*, 50, 398-402.
- Kennard, M. L., Meisen, A.,** (1983) Gas Chromatographic Technique for analysing Partially Degraded Diethanolamine Solutions, *Journal of Chromatography*, 267, 373-380

- Kentish, S., Hooper, B., Stevens, G., Perera, J. & Qiao, G.** (2006) An Overview of Technologies for Carbon Capture, *AIE National Conference –Technologies for Carbon Captur.*
- Ko, J. J. & Li, M. H.** (2000) Kinetics of absorption of carbon dioxide into solutions of N-methyldiethanolamine+water. *Chemical Engineering Science*, 55, 4139-4147
- Kongstein O. E. & Schmid B.** (2010) Corrosion of Stainless Steel in Amine solutions for Carbon Dioxide Capture, *218th ECS Meeting, Abstract 1249*
- Lawal, O., Bello, A. & Idem, R.** (2005) The role of methyl diethanolamine (MDEA) in preventing the oxidative degradation of CO₂ loaded and concentrated aqueous monoethanolamine (MEA)-MDEA blends during CO₂ absorption from flue gases. *Industrial and Engineering Chemistry Research*, 44, 1874-1896.
- Lawal, A. O. & Idem, R. O.** (2006) Kinetics of the oxidative degradation of CO₂ loaded and concentrated aqueous MEA-MDEA blends during CO₂ absorption from flue gas streams. *Industrial and Engineering Chemistry Research*, 45, 2601-2607.
- Lawson, J. D. & Garst, A. W.** (1976) Gas Sweetening Data: Equilibrium solubility of hydrogen sulphide and carbon dioxide in aqueous Monoethanolamine and aqueous diethanolamine solutions. *Journal of Chemical and Engineering Data*, 21, 1, 20-30.
- Lee, J. I., Otto, F. D. & Mather, A. E.** (1976) Equilibrium between carbon dioxide and aqueous Monoethanolamine solutions. *J. appl. Chem. Biotechnol.*, 26, 541-549.
- Lepaumier, H., Picq, D. & Carrette, P. L.** (2008) Degradation Study of new solvents for CO₂ capture in post-combustion. *9th International Conference on Greenhouse Gas Control Technologies*, Washington DC.
- Lepaumier, H., Picq, D. & Carrette, P. L.** (2009) Degradation Study of new solvents for CO₂ capture in post-combustion. *Energy Procedia*, 1, 893-900
- Lepaumier, H., Picq, D. & Carrette, P. L.** (2009) New Amines for CO₂ Capture. I. Mechanisms of Amine Degradation in the Presence of CO₂. *Ind. Eng. Res.*, 48, (9061-9067
- Lepaumier, H., Picq, D. & Carrette, P. L.** (2009) New Amines for CO₂ Capture. II. New Amines for CO₂ Capture. II. Oxidative Degradation Mechanisms. *Ind. Eng. Re.*, 48, 9067-9075
- Lepaumier, H., Picq, D. & Carrette, P. L.** (2010) New Amines for CO₂ Capture. III. Effect of Alkyl Chain Length between Amine Functions on Polyamines Degradation. *Ind. Eng. Re.*, 49, 4553-4560
- Liao, C. H. & Li, M. H.** (2002) Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + N-methyldiethanolamine. *Chemical Engineering Science*, 57, 4569-4582
- Lyudkovskaya M. A. and Leibush A. G.** (1949) Solubility of Carbon Dioxide in Solutions of Ethanolamines under Pressure. *Zh. Prik. Khim.*, 22, 558.
- Ma'mum, S., Nilsen, R. & Svendsen H. F.** (2005) Solubility of carbon dioxide in 30 % Monoethanolamine and 50 % methyldiethanolamine solutions. *J. Chem. Eng. Data*, 50, 630-634.
- Mandal, B. P. & Bandyopadhyay, S. S.** (2006) Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and monoethanolamine. *Chemical Engineering Science*, 61, 5440-5447.
- March J.** (1992) *Advanced Organic Chemistry: Reaction mechanisms and structure.* Wiley
- Mason, J. W. and Dodge, B. F.** (1936) Equilibrium Absorption of Carbon Dioxide by Solutions of the Ethanolamines. *Trans. AIChE*, 32, 27.
- McCann N., Phan D., Wang X., Conway W., Burns R., Attalla M., Puxty G. and Maeder M.** (2009) Kinetics of Carbamate Formation from CO₂(aq), Carbonate

Species, and Monoethanolamine in Aqueous Solution. *J. Phys. Chem.*, 113, 5022-5029

Murrieta-Guevara F., Rebolledo-Libretos E. and Trejo A. (1993) Gas Solubility of Carbon Dioxide and Hydrogen Sulfide in Mixtures of Sulfolane with Monoethanolamine, *Fluid Phase Equilibria*, 86, 225-231

Nasir, P. and Mather, A. E. (1977) The Measurement and Prediction of the Solubility of Gases in Monoethanolamine Solutions at Low Partial Pressures, *Can. J. Chem. Eng.*, 55,715-716

Oikawa K., Yongsirib C., Takeda K. and Harimotoa T., (2003) Seawater Flue Gas Desulphurization: Its Technical Implications and Performance results, *Environmental Progress*, 22, 1, 67-73.

Oyeanean, B. A. & Rochelle, G. T. (2006) Energy Performance of Stripper Configurations for CO₂ Capture by Aqueous Amines, *Ind. & Eng. Chem. Res.*, 45 (8), 2457-2464.

Polderman, L. D. & Dillon C.P. (1955) Why monoethanolamine solution breaks down in gas treating service” *Proc. Gas Conditioning Conf*: 49-56

Ramachandran, N., Aboudheir, A., Idem, R., Tontiwachwuthikul, P., (2006) Kinetics of the Absorption of CO₂ into Mixed Aqueous Loaded Solutions of Monoethanolamine and Methyldiethanolamine, *Ind. Eng. Chem. Res.*, 45, 2608-2616

Ricci L. (2004) Separation Techniques 2: Gas/Liquid/Solid System. McGraw-Hill Publications Co.

Rinker, E. B., Ashour, S. S. & Sandall, O. C. (2000) Absorption of Carbon Dioxide into Aqueous blends of Diethanolamine and Methyldiethanolamine, *Ind. Eng. Chem. Res.*, 39, 4346-4356

Robbins G. D & Bullin J. A. (1984) Analysis of Amine Solutions by Gas Chromatography, *Energy Progress*, 229-232.

Rochelle, G. T. (2007) CO₂ Capture by Aqueous Absorption/Stripping, *Presented at ABMA Annual Meeting*.

Rooney, P. C., Dupart, M.S., Bacon, T. R. (1998) Oxygen’s Role in Alkaloamine Degradation, Hydrocarbon Processes, *Int Ed.*, 77 (7), 109-113

Rouessac F. & Rouessac A. (2004) Chemical Analysis: Modern Instrumentation Methods and Techniques. 4th edition, Wiley

Saha, A. K., Bishwas, A. K. & Bandyopadhyay, S. S. (1999) Absorption of CO₂ in a Sterically Hindered Amines: modeling absorption in a mechanically agitated contactor. *Separation and Purification Technology*, 15, 101-112.

Sartori, G. & Savage, D. W. (1983) Sterically Hindered Amines For CO₂ Removal From Gases. *Industrial & Engineering Chemistry, Fundamentals*, 22, 239-249

Scheiman M.A. (1962) A review of Monoethanolamine Chemistry. Reproduced by the Armed services Technical Information Agency.

Sexton, A. J. & Rochelle, G. T. (2006) Oxidation products of amines in CO₂ capture. *8th International Conference on Greenhouse Gas Control Technologies*, Trondheim, Norway.

Sexton, A. J. & Rochelle, G. T. (2008) Catalysts and inhibitors for MEA oxidation. *9th International Conference on Greenhouse Gas Control Technologies*, Washington DC.

Shreve R.N. & Brink J. A., (1977) Chemical Process Industries. 4th edition, McGraw-Hill Publications Co.

Skoog D. A., West D. M & Holler F. J., Analytical Chemistry. 7th edition, Saunders College Publishing

- Shen, K.-P. & Li, M.-H.** (1992) Solubility of carbon dioxide in aqueous mixtures of Monoethanolamine with methyldiethanolamine. *J. Chem. Eng. Data*, 37, 96-100.
- Skoog D. A., West D. M & Holler F. J,** Analytical Chemistry. 7th edition, Saunders College Publishing.
- Strazisar, B. R., Anderson, R. R. & White, C. M.** (2001) Degradation of Monoethanolamine used in carbon dioxide capture from flue gas of a coal fired electric power generating station. *J. Energy & Environ. Res.*, 1(1), 32-40.
- Stratizisar, B. R., Anderson, R. R. & White, C. M.** (2003) Degradations pathways for monoethanolamine in a CO₂ capture facility, *Energy & Fuels*, 17, 1034-1039.
- Supap, T., Idem, R., Tontiwachwuthikul, P. & Saiwan, C.** (2006) Analysis of monoethanolamine and its oxidative degradation products during CO₂ absorption from flue gases: A comparative study of GC-MS, HPLC-RID, and CE-DAD analytical techniques and possible optimum combinations. *Industrial and Engineering Chemistry Research*, 45, 2437-2451.
- Supap, T., Idem, R., Tontiwachwuthikul, P. & Saiwan, C.** (2009) Kinetics of sulphur dioxide -and oxygen- induced degradation of monoethanolamine solution during CO₂ Absorption from Industrial Flue Gas Streams, *International Journal of Greenhouse Gas Control*, 3, 133-142.
- Tantathapanichakoon W., Veawab A., McGarvey B.,** (2006) Electrochemical Investigation on the Effect of Heat-Stable Salts on Corrosion in CO₂ Capture Plants Using Aqueous Solution of MEA, *Ind. Chem. Res.*, 45, 2586-2593.
- Uyanga, I. J. & Idem R. O.** (2007) Studies of SO₂- and O₂- induced degradation of aqueous MEA during CO₂ capture from power plant flue gas streams, *Industrial and Engineering Chemistry Research*, 46(8), 2558-2566.
- Vrachnos, A., Kontogeorgis, G. & Voutsas, E.** (2006) Thermodynamic modelling of acidic gas solubility in aqueous solutions of MEA, MDEA and MEA-MDEA blends, *Ind. Eng. Chem. Res.* 45, 5148-5154.
- Versteeg, G.F.,** (2007) CO₂ capture from power plants Part I. A parametric study of the technical performance based on monoethanolamine, *International journal of greenhouse gas control*, 1, 37 – 46
- Wong, S. & Bioletti, R.** (2002) Carbon Dioxide Separation Technologies - ARC. *Inter-American Association of Sanitary and Environmental Engineering Technical Brochure 1*
- Yavzikova N. V., Zelenskaya L. G. and Balyasnikova L.V.** (1975) Mechanism of Side Reactions during Removal of Carbon Dioxide from Gases by Treatment with Monoethanolamine, *Journal of Applied Chemistry of the USSR*, 48, 674-676
- Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R. B., Bland, A. E. & Wright, I.** (2007) Progress in Carbon Dioxide Separation and Capture: A review, *Journal of Environmental Sciences*, 20 (1), 14-27
- Yeh, A. C. & Bai, H.,** (1999) Comparison of Ammonia and Monoethanolamine Solvents to Reduce CO₂ Greenhouse Gas Emissions, *Sci. Total Environ.* 228, 121–133
- Yeh, J. T., Pennline, W. H.** (2001) Study of CO₂ Absorption and Desorption in a Packed Column, *Energy & Fuels*, 15, 274-278
- Yeh, J. T., Resnik, K. P., Rygle, K. & Pennline, H.W** (2006) Semi-batch absorption and regeneration studies for CO₂ capture by aqueous ammonia, *Fuel Processing Technology*, 86 (14-15), 1533-1546

6 FIGURES

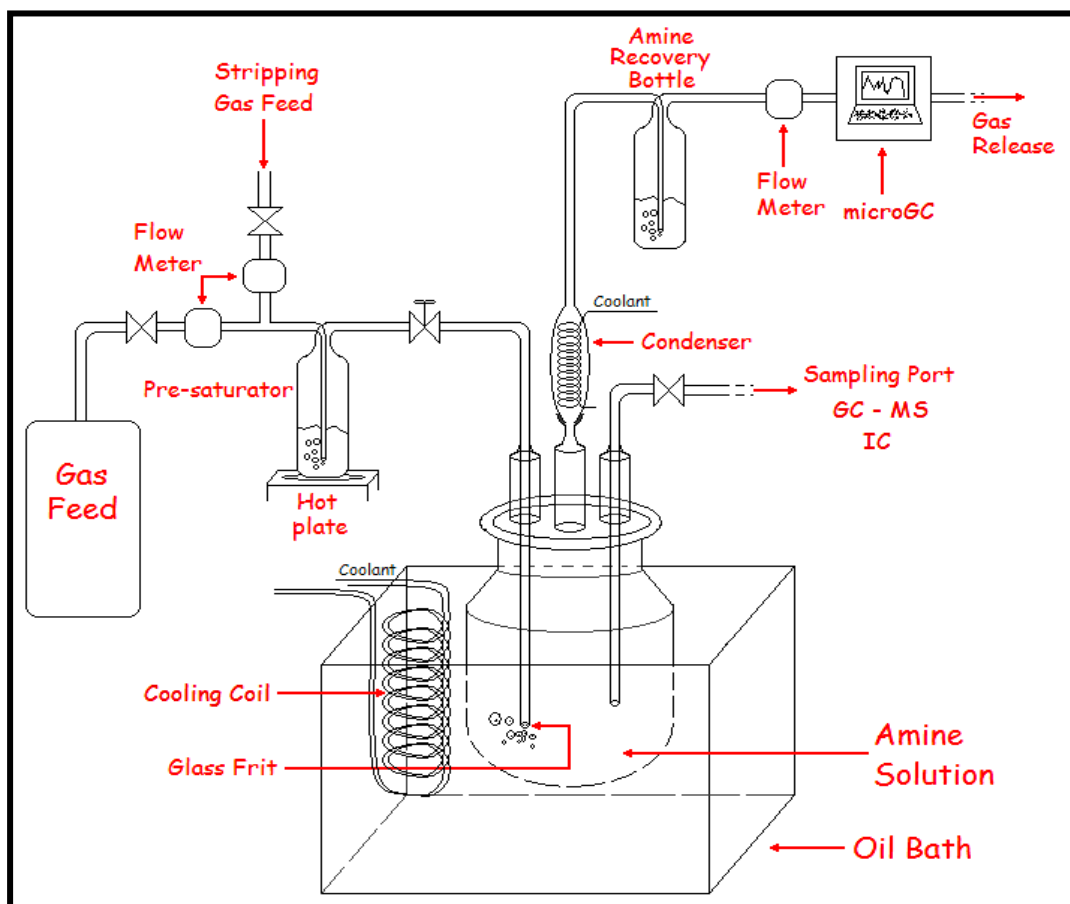


Figure 2.1 Schematic of the gas absorption and desorption rig

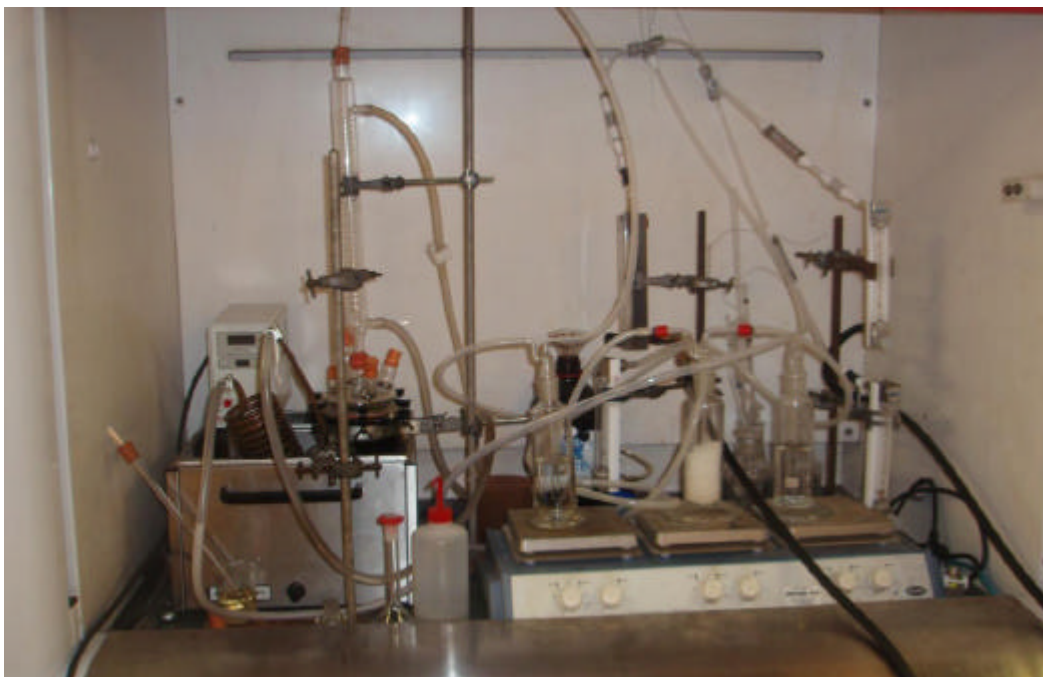


Figure 2.2 Photograph of the gas absorption and desorption rig



Figure 2.3 Photograph of the thermal degradation vessels in the oven

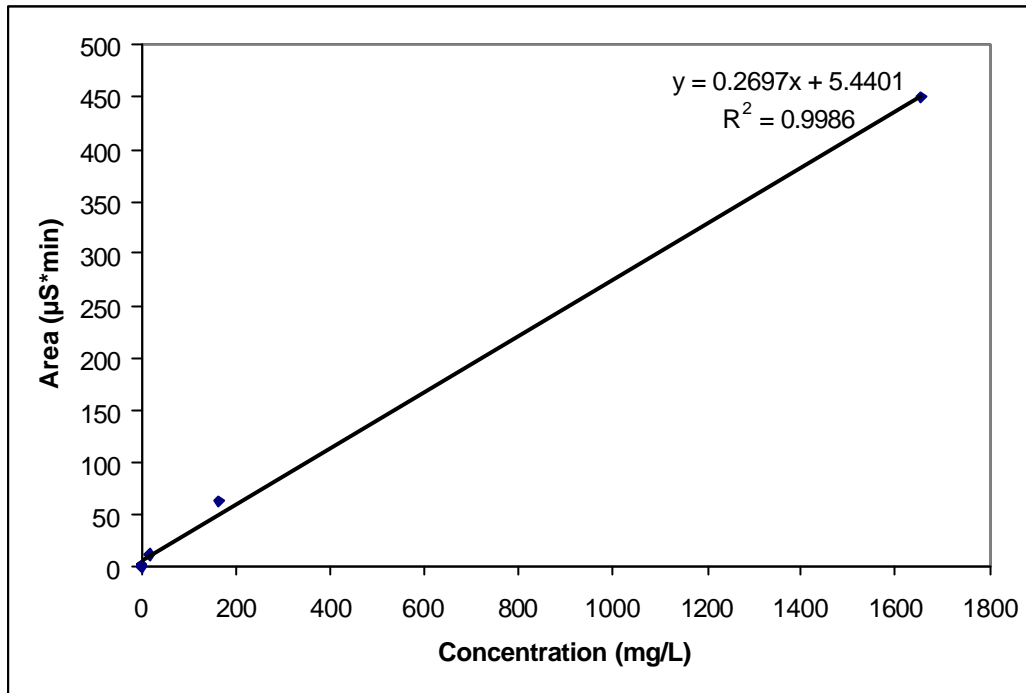


Figure 3.1 Calibration curve for oxalate ion in the IC

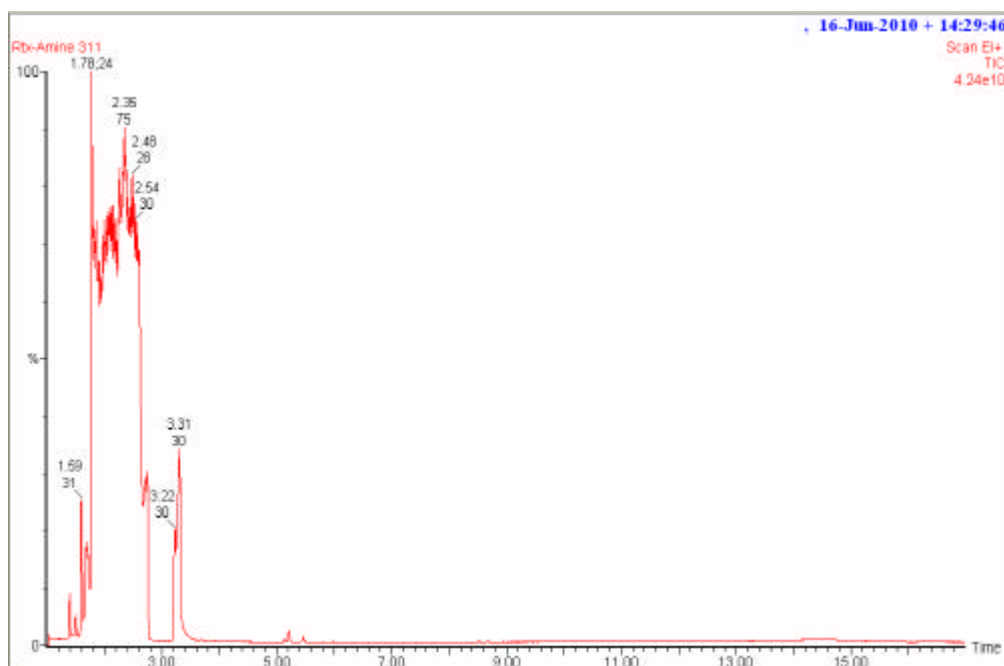


Figure 3.2 Response from the GC-MS for pure MEA in water after being extracted into diethyl ether

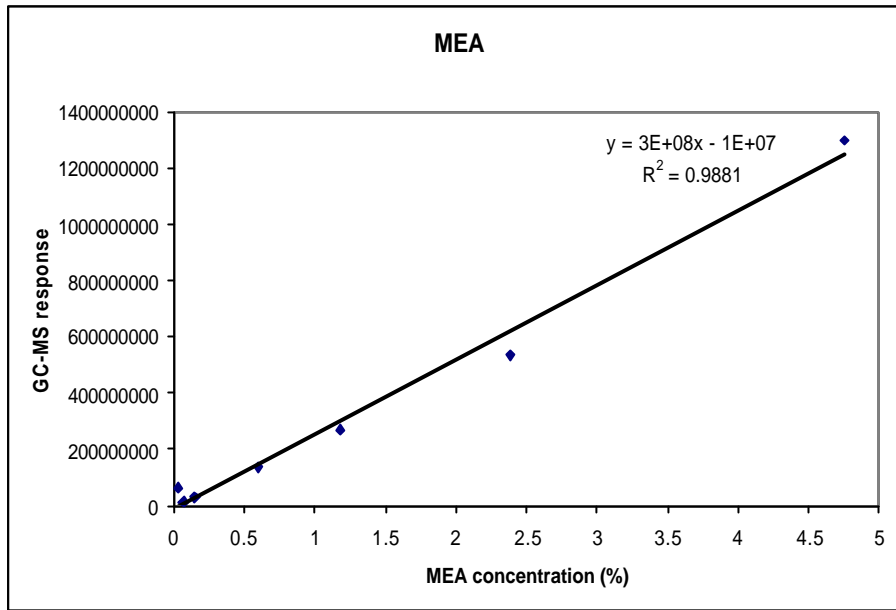


Figure 3.3 Calibration curve for the GC-MS for pure MEA in diethyl ether

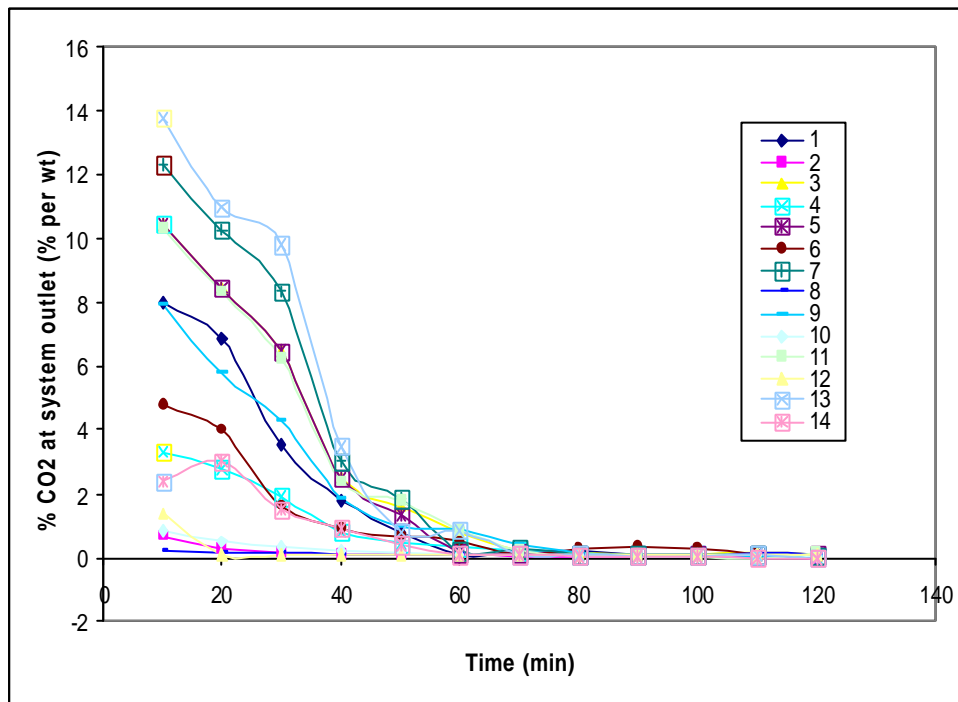


Figure 3.4 CO₂ percentages at rig's outlet during absorption for the initial degradation attempts with O₂

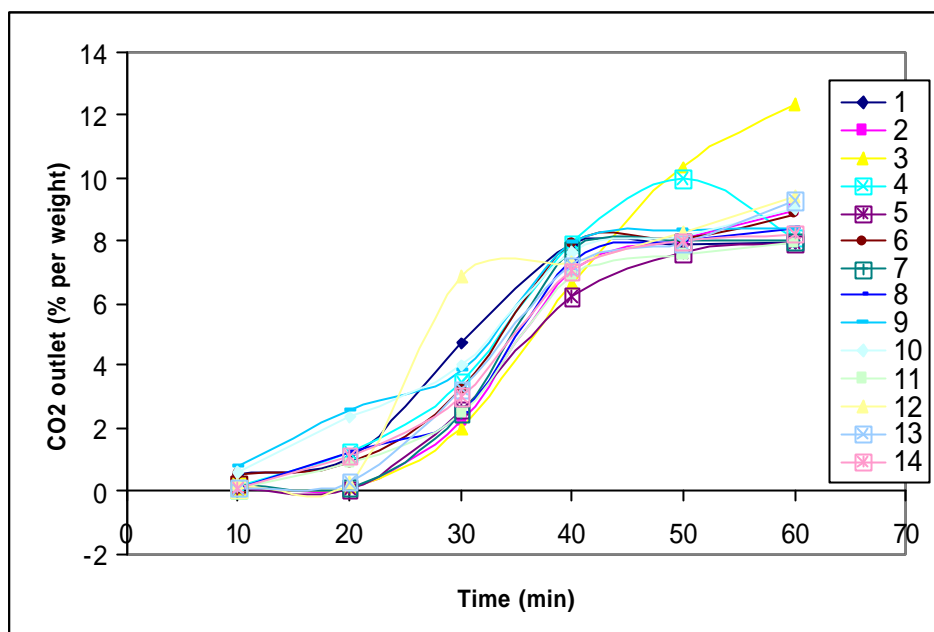


Figure 3.5 CO₂ percentages at rig's outlet during stripping for the initial degradation attempts with O₂

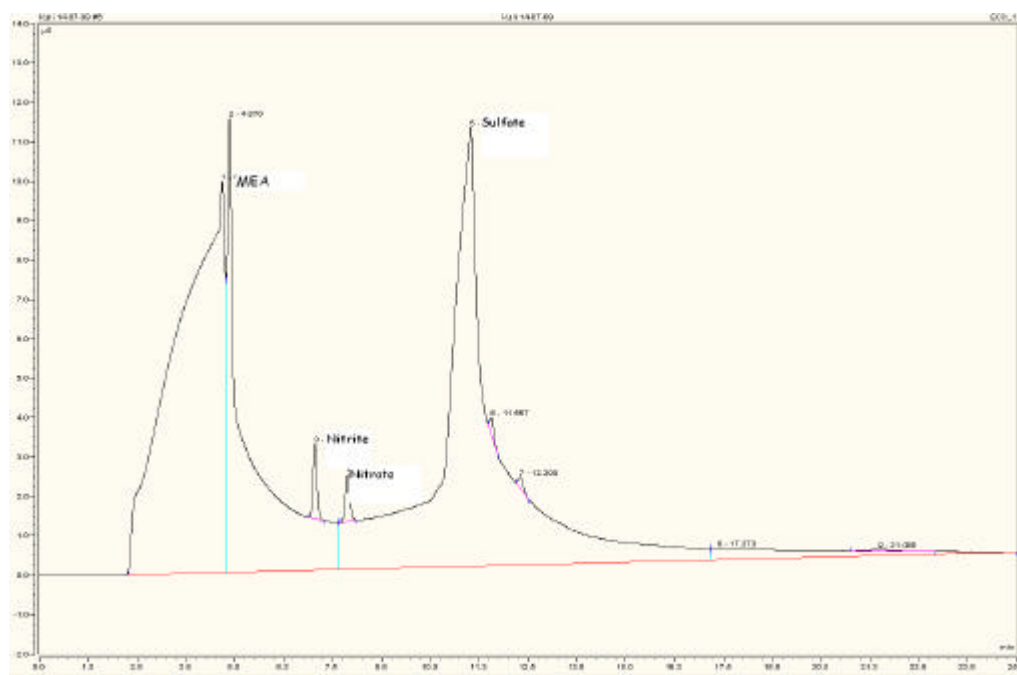


Figure 3.6 IC response of the 5 molal aqueous MEA solution after 14 repeated cycles of absorption and stripping in the presence of O₂.

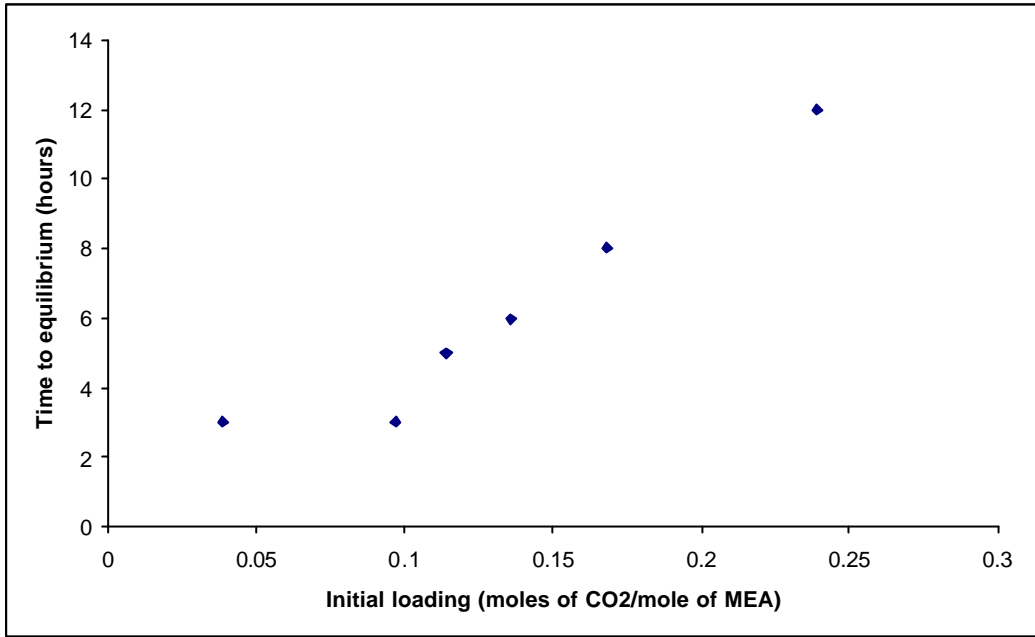


Figure 3.7 Time to equilibrium versus the initial CO₂ molar loading of the MEA solution, at 100 °C.

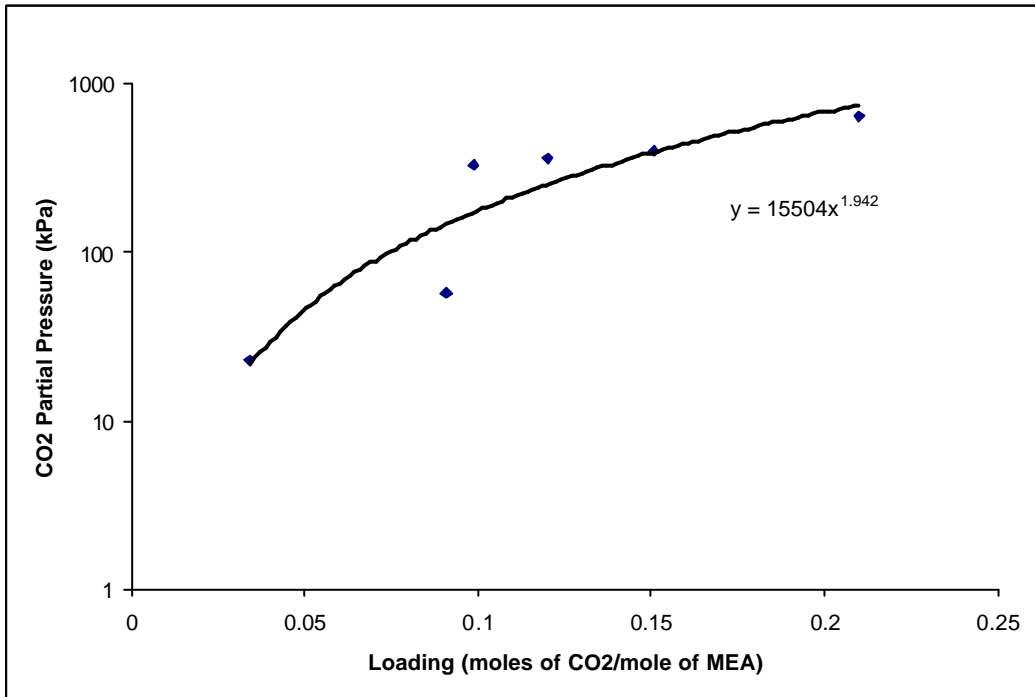


Figure 3.8 CO₂ partial pressure versus CO₂ loading for 30 % wt aqueous MEA solution at 100 °C

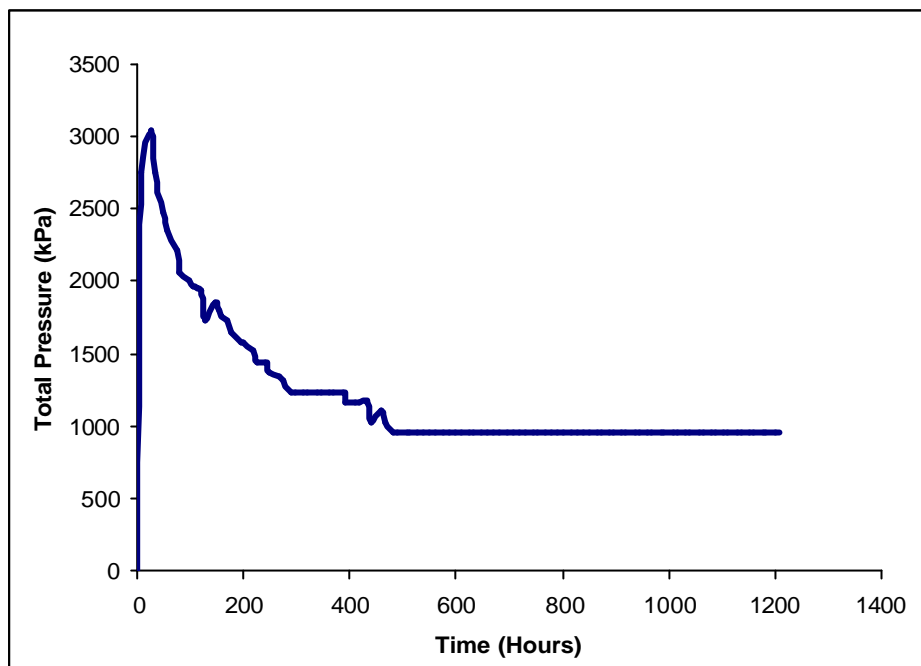


Figure 3.9 Total headspace pressure – “lean” loading test

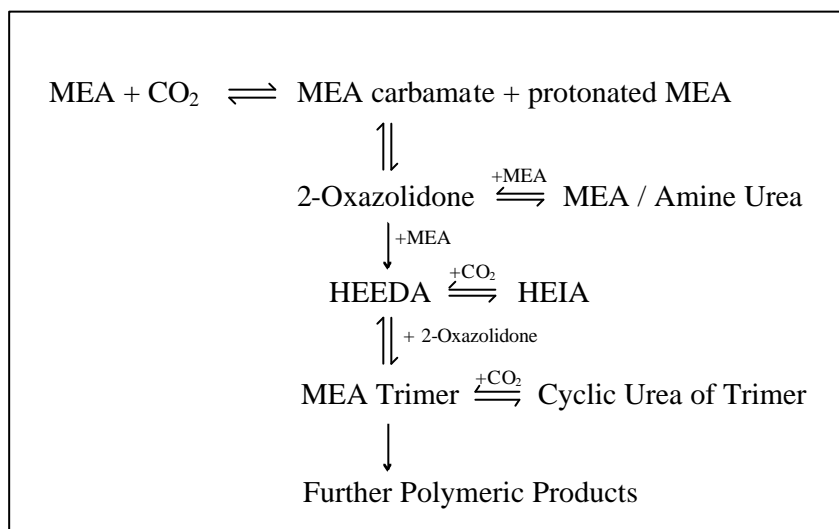


Figure 3.10 Schematic of the pathway of formation of MEA carbamate polymerization degradation proposed by Davies (2009)

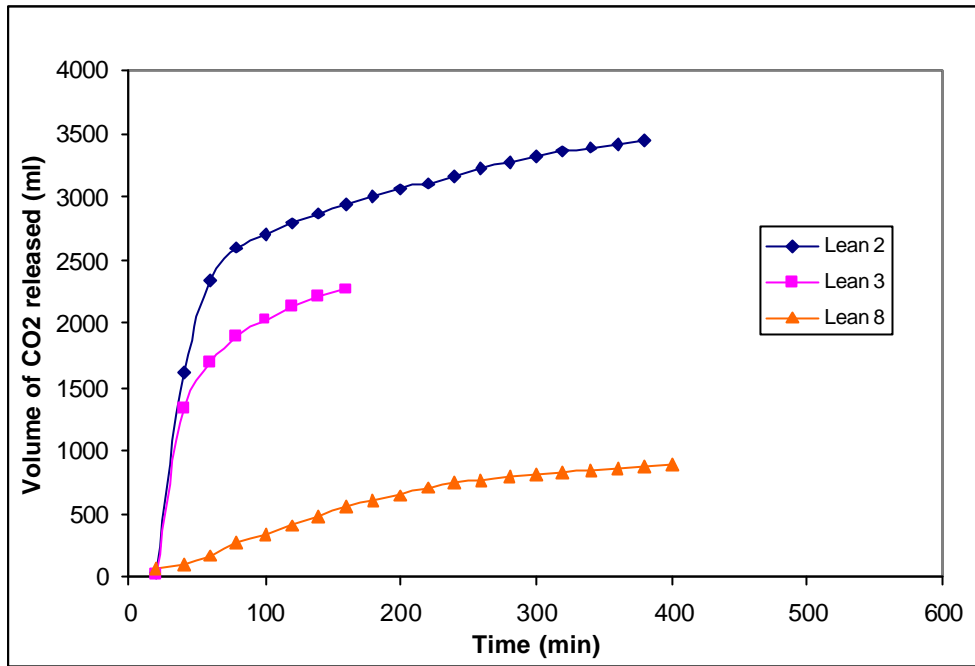


Figure 3.11 Cumulative CO₂ volume released during the 1st stripping – “lean” loading test

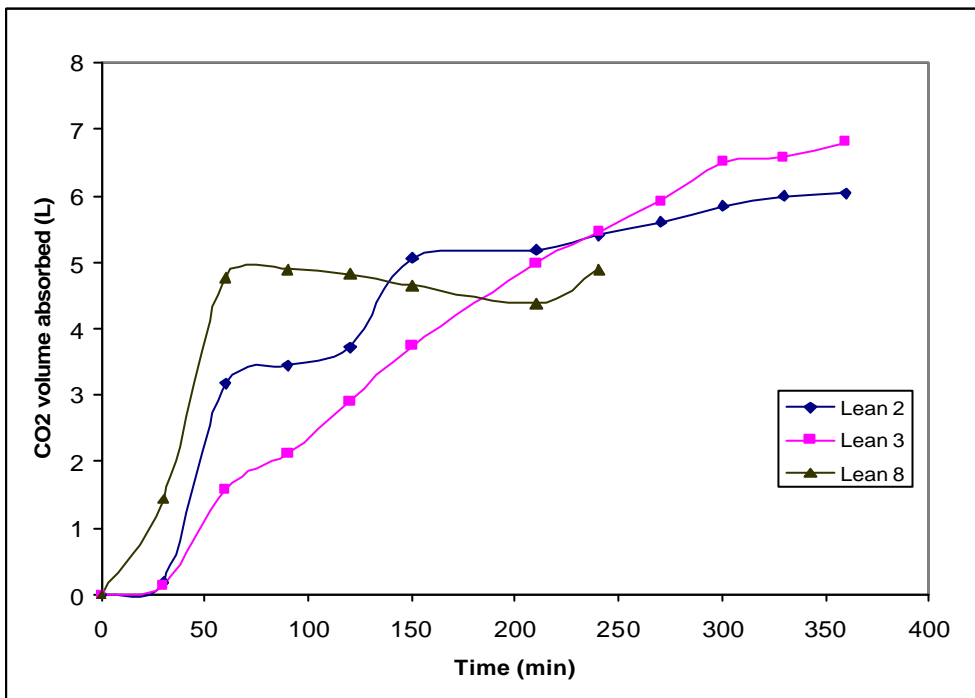


Figure 3.12 Cumulative volume of CO₂ absorbed – “lean” loading test

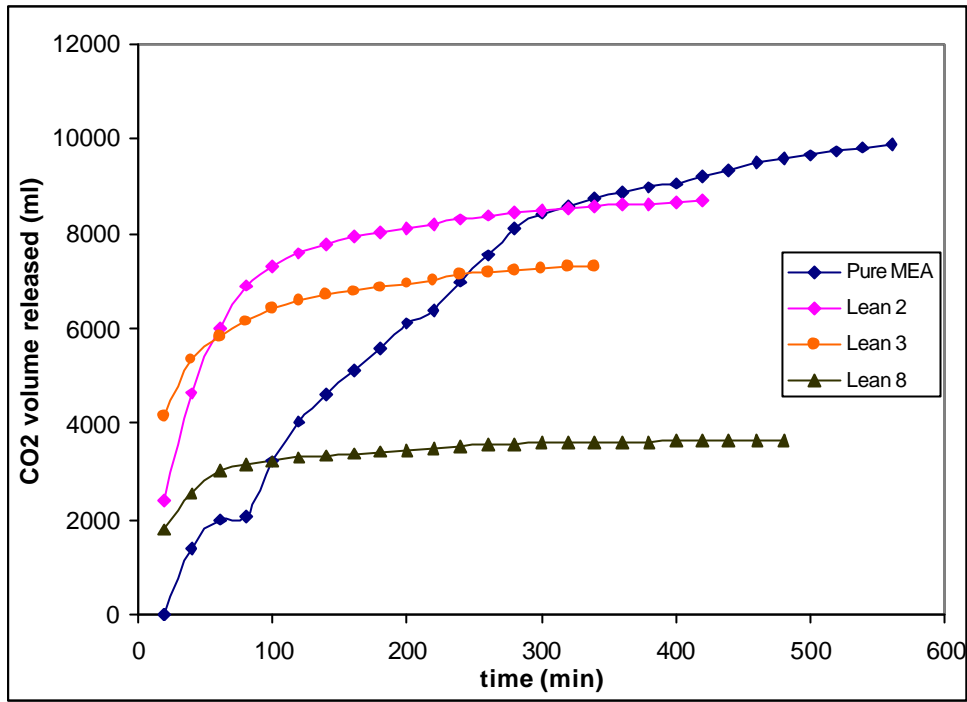


Figure 3.13 Cumulative volume of CO₂ released – “lean” loading test

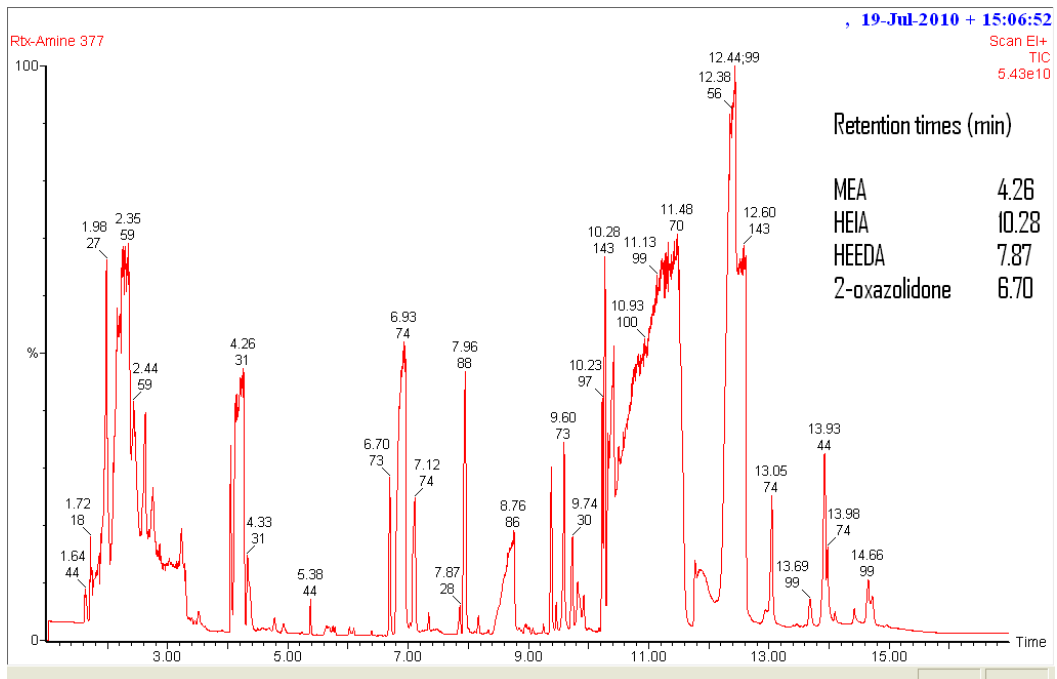


Figure 3.14 GC-MS response for the 2 weeks degraded sample – “lean” loading test

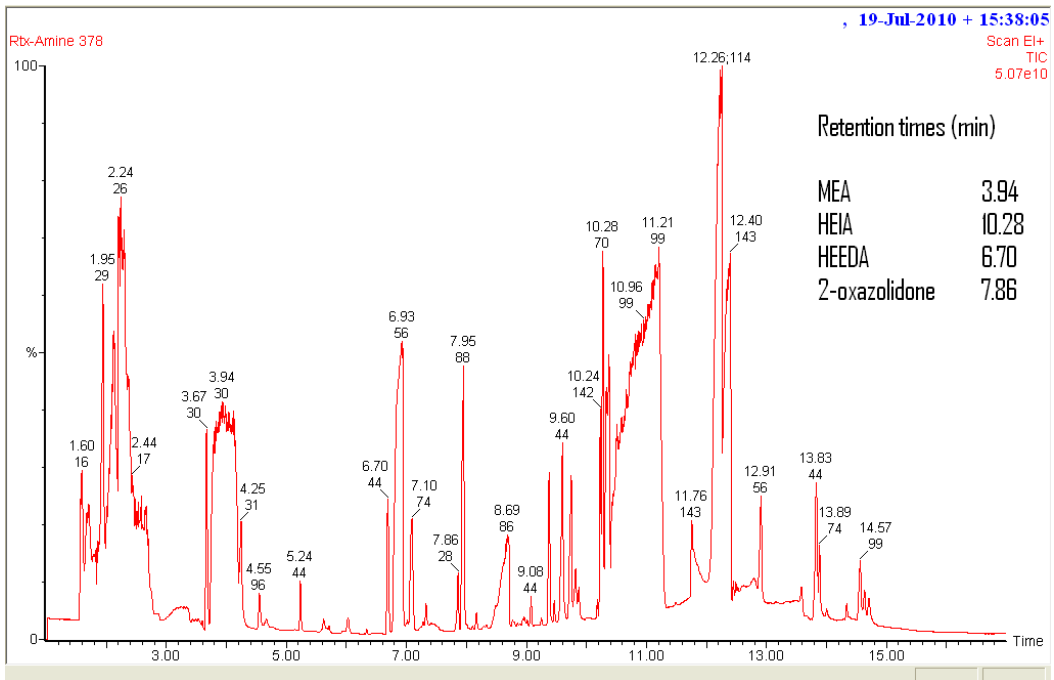


Figure 3.15 GC-MS response for the 3 weeks degraded sample – “lean” loading test

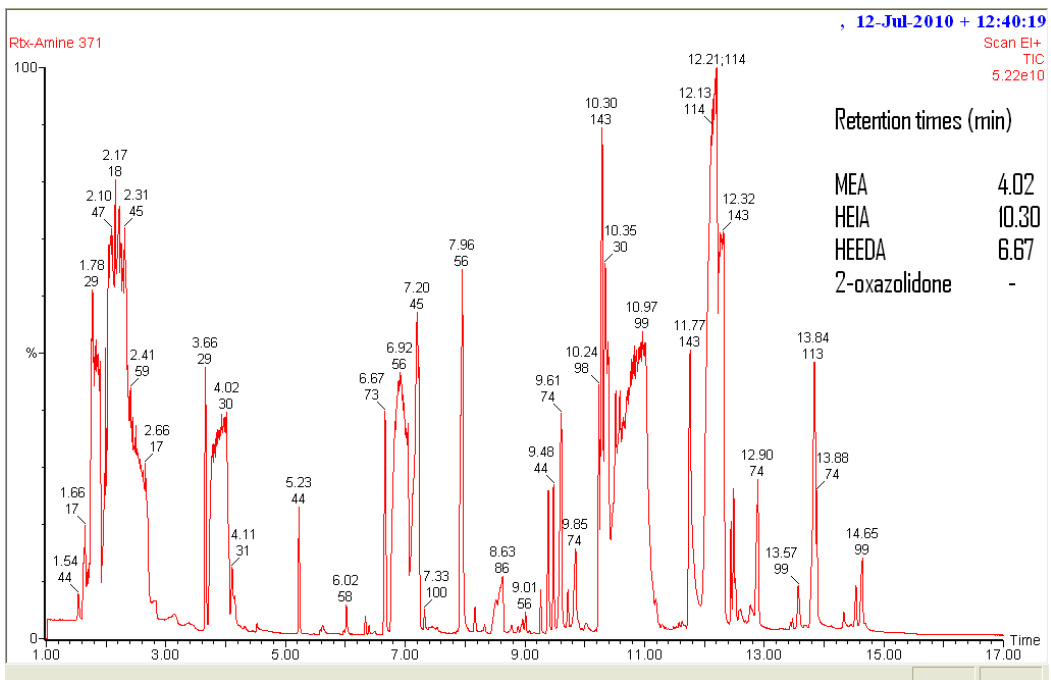


Figure 3.16 GC-MS response for the 8 weeks degraded sample – “lean” loading test

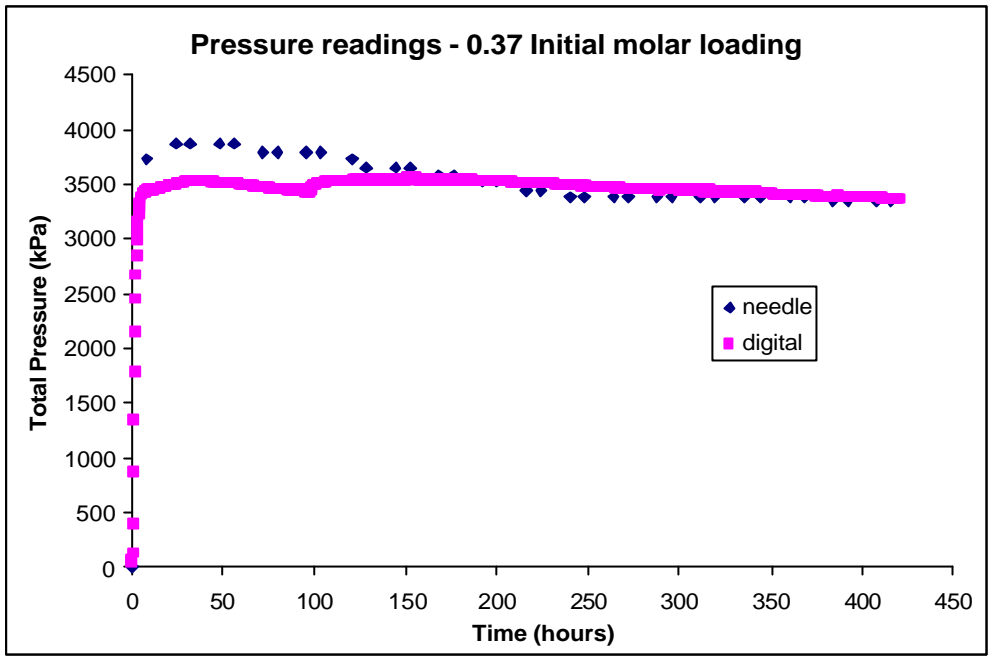


Figure 3.17 Total headspace pressure measured in two pressure vessels – “rich” loading test

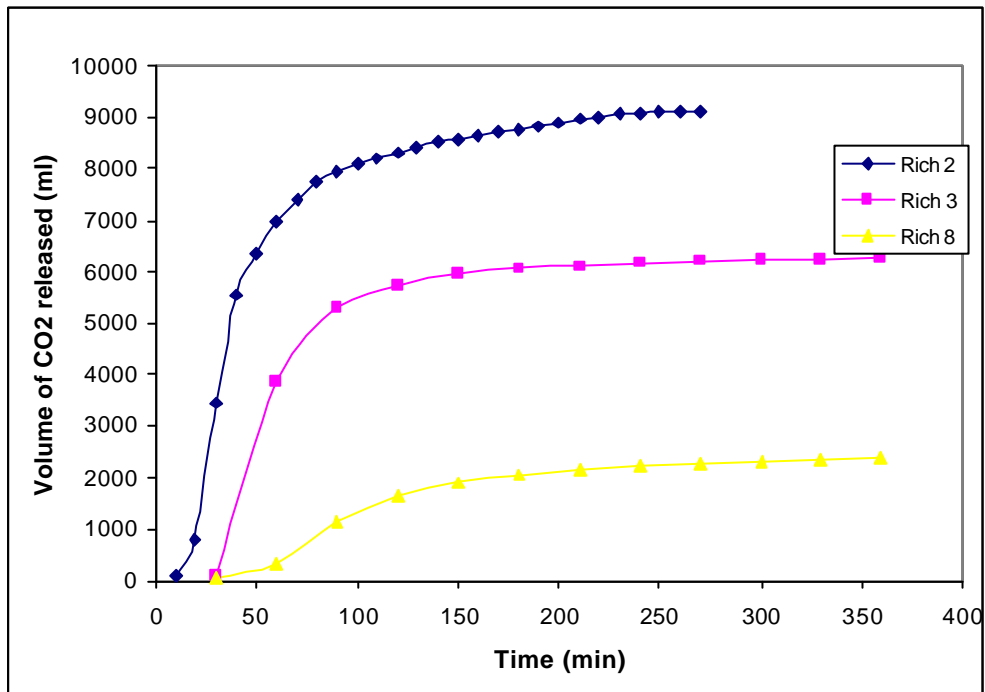


Figure 3.18 Cumulative CO₂ volume released during the 1st stripping – “rich” loading test

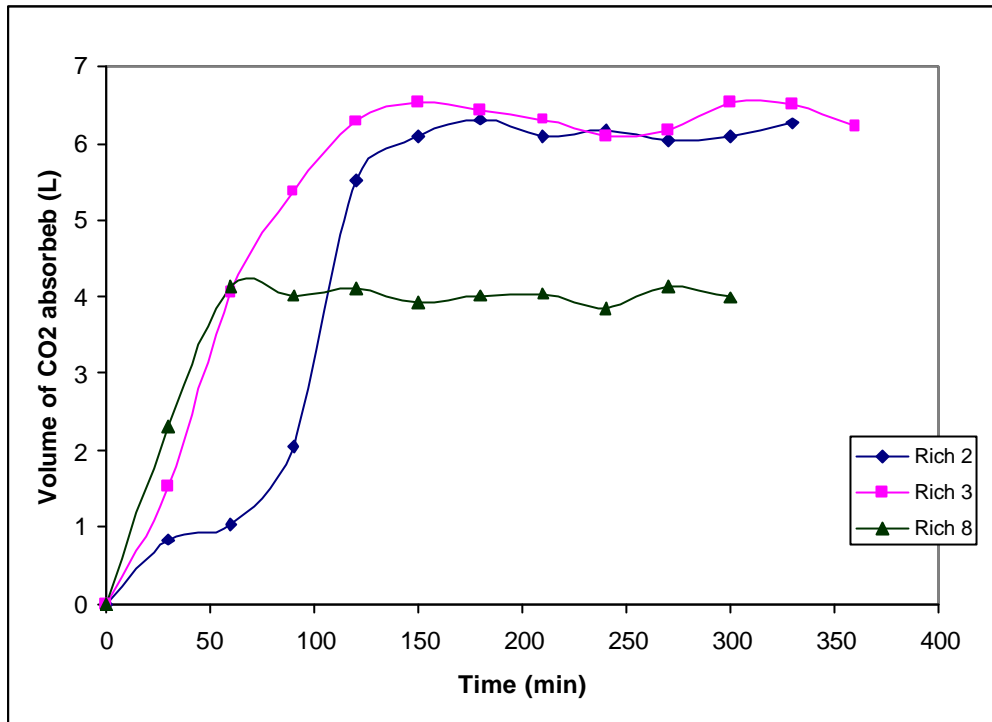


Figure 3.19 Cumulative volume of CO₂ absorbed – “rich” loading test

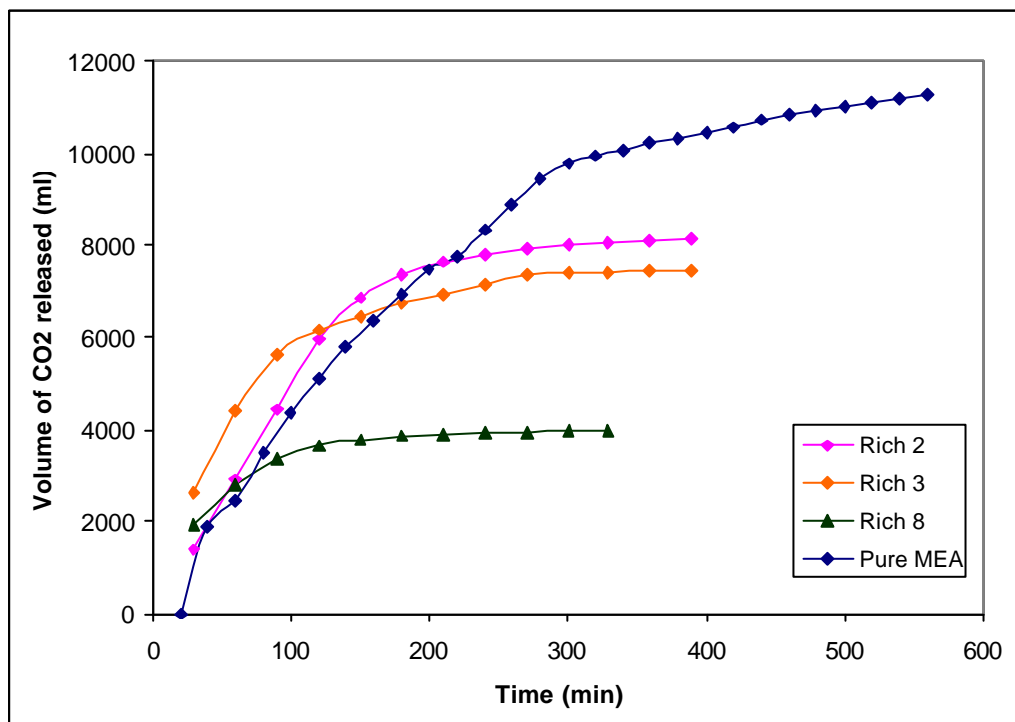


Figure 3.20 Cumulative volume of CO₂ released – “rich” loading test

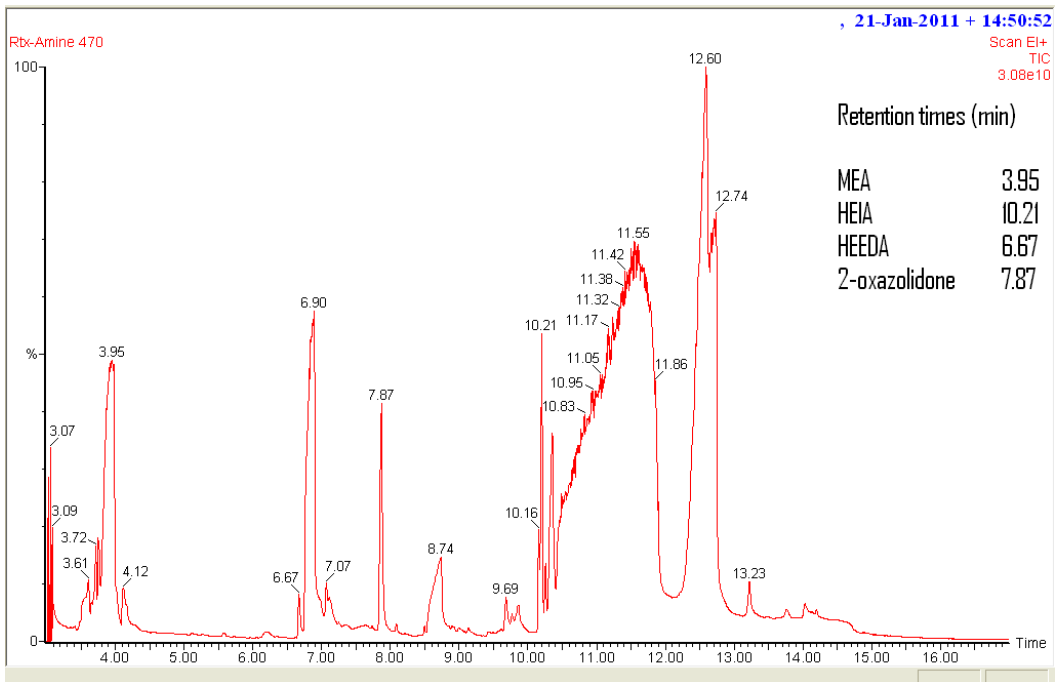


Figure 3.21 GC-MS response for the 2 weeks degraded sample – “rich” loading test

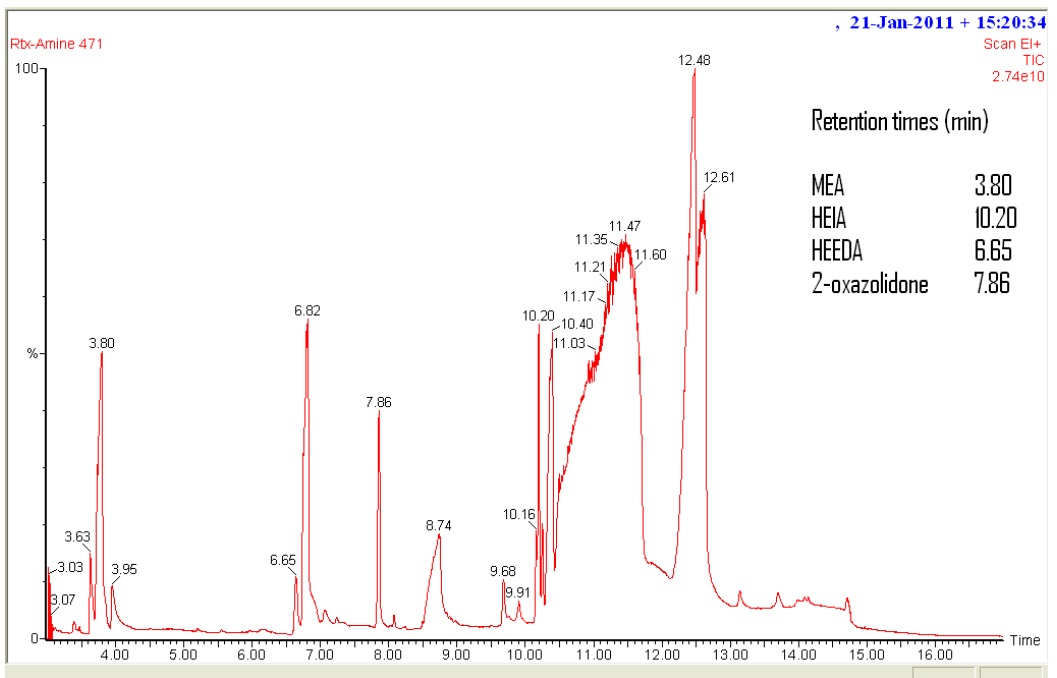


Figure 3.22 GC-MS response for the 3 weeks degraded sample – “rich” loading test

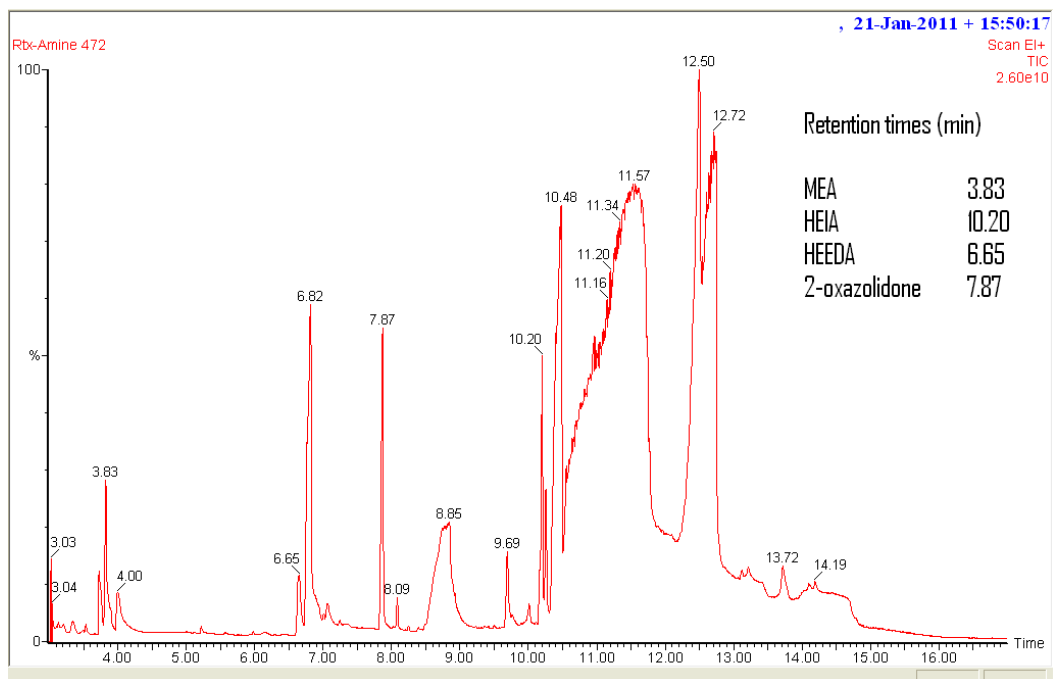


Figure 3.23 GC-MS response for the 8 weeks degraded sample – “rich” loading test