ORCA – Online Research @ Cardiff

Citation for final published version:

Zoannou, Kali-Stella, Sapsford, Devin James and Griffiths, Anthony John 2013. Thermal degradation of monoethanolamine and its effect on CO2 capture capacity. International Journal of Greenhouse Gas Control 17 , pp. 423-430. 10.1016/j.ijggc.2013.05.026

Publishers page: http://dx.doi.org/10.1016/j.ijggc.2013.05.026

Zoannou, K.S., Sapsford, D.J. and Griffiths, A.J., 2013. Thermal degradation of monoethanolamine and its effect on CO_2 capture capacity. *International Journal of Greenhouse Gas Control*, 17, pp.423-430.

Thermal degradation of monoethanolamine and its effect on CO_2 capture capacity

K.S. Zoannou[a], D.J. Sapsford[a], A.J. Griffiths[a]

[a]Cardiff School of Engineering, Cardiff University, Cardiff, CF24 3AA, UK

Abstract

Amine scrubbing is a proven technology in the oil and gas industries. Its use in coal fired power plants is not fully understood and the likelihood of solvent degradation is high. Decreased absorption efficiency, undesirable by-products and the environmental impact of their disposal are the main consequences. In the present study, samples of monoethanolamine were thermally degraded, at 160◦C for between 2 and 8 weeks, and their CO_2 removal capacity deterioration was determined. The findings show that thermal degradation at 160◦C for 8 weeks reduced monoethanolamine concentration by 95%, but the remaining solvent still retained 22% of its capacity to remove CO_2, probably due to the capacity of some of the degradation products to remove CO_2. Therefore, the requirement for monoethanolamine make-up in operational amine scrubbing systems may not be quite as serious as initially believed. A 20% higher MEA loss was determined in the samples with 0.37 initial CO_2 loading (mol CO_2/mol MEA). 2-Oxazolidone, N-(2-hydroxyethyl)-ethylenediamine and 1-(2-hydroxyethyl)-2-imidazolidinone were identified as the major monoethanolamine degradation products, the latter being indicated as the most stable product with concentrations of up to 17% (v/v). Corrosion (1.95 mm/year) of the stainless steel (type 316) equipment, used during the experiments, was also observed.

1. Introduction

Amine scrubbing has been an established technology for acid gas removal in the chemical and oil industries for many decades. Thus, it is considered that it can be readily implemented on a large scale at existing power plants for CO_2 removal (Mangalapally et al., 2009). Aqueous solutions of 30% (w/v) monoethanolamine (MEA) are the reference solvents for such processes (Moser et al., 2011). There are numerous technical and environmental challenges that are encountered during the application of MEA in industrial CO_2-scrubbing systems. During the absorption-stripping process, considerable solvent losses occur. Amine solvents are very volatile and as a result are likely to evaporate from the liquid into the gas phase, escape to the atmosphere and react producing environmentally hazardous compounds (Nguyen et al., 2011). Moreover, the irreversible reactions which may occur during the process result in the accumulation of degradation products in the solvent and the reduction of the active MEA content. Hence, there is a requirement for partial or complete replacement of the solvent in order to maintain the plant efficiency (Abdi, 1997). Often the spent degraded solutions contain about 80% of the original amine (Abdi, 1997) and as a result, in addition to the environmental impact of the degraded solvent disposal, pure solvent is also wasted. Islam et al. (2011) reports that the replacement costs of the solvent in an MEA plant are estimated to be around 4% of the total costs of carbon sequestration. Finally, as reported by Strazisar et al. (2003), the solvent make up requirements due to solvent degradation are calculated to be around 2.2 kg of MEA solvent per tonne CO_2 captured. The generated degradation products are believed to be responsible for equipment corrosion, foaming, fouling and an increase in the solvent's viscosity. Additional equipment is needed in order to remove the by-products generated during the procedure and these degradation products are disposed as hazardous chemical wastes (Islam et al., 2011). Therefore, there is an impact on the process economics and the environmental impact of the disposal of the liquid and solid wastes recovered.

There is a requirement for further research on the rates, mechanisms and products of the degradation of MEA in conditions likely to be encountered in industrial application of CO_2 scrubbers. MEA can be degraded during the process principally due to either oxidative or thermal degradation. Oxidative degradation is caused due to the presence of O_2 (typically > 5%) in coal fired power station flue gas and leads to MEA degradation during the absorption stage, resulting in the formation of, mainly, heat-stable salts (Sexton and Rochelle, 2008).

The presence of SO and SO_2 as well as NO_x can also cause the formation of heat stable corrosive salts (Brakstad et al., 2010). Thermal degradation occurs in the presence of CO_2 at temperatures encountered in the cross exchanger, stripper and the thermal reclaiming unit and causes the formation of large polymeric compounds (Davies, 2009). In recent pilot plant studies, Lepaumier et al. (2011)

demonstrate that in degraded MEA samples from Esbjerg amine scrubbing plant, oxidative degradation was more dominant than thermal degradation. HEIA and 2-oxazolidone were detected in the pilot plant samples with the latter being reported as an oxidative degradation product, common with thermal degradation. Moreover, Moser et al. (2011) suggest that, even though carbamate polymerisation products were detected in samples from a pilot plant at Niederaussem, oxidative degradation products were detected at higher concentrations after 5000 h of operation. However, in both the aforementioned studies, neither solvent reclaiming units nor oxidation inhibitors were used in the pilot plants described. Reynolds et al. (2012) also report that solvents are not usually reclaimed during pilot trials. According to Davis (2009) and Reynolds et al. (2012) thermal degradation by carbamate polymerisation occurs at temperatures also encountered in thermal reclaiming units. According to Reynolds et al. (2012) there is some concern that thermal degradation products might act as chelators that can increase the severity of corrosion.

The identification and quantification of the thermal degradation products generated within an MEA-based CO_2 scrubbing system, the chemistry of degradation and the pathways of formation of degradation products are not yet fully understood and thus require further research. Furthermore, with a better understanding of the mechanisms the effect of the process parameters on solvent degradation can be further assessed in order to control degradation and potentially reduce the energy consumption and costs of the process. Finally, understanding how thermal degradation occurs may help in developing new stripper configurations, as according to Davis (2009) stripping is the largest economic factor in the capture of CO_2.

A number of researchers performed studies on the MEA loss due to thermal degradation at temperatures below 200 ◦C (Polderman and Dillon, 1955). Davis (2009) and Eide-Haugmo et al. (2011) suggest that the MEA loss and the percentage of formation of the degradation products is dependent on the temperature, the CO_2 loading and the MEA initial concentration. The largest MEA loss is reported by Davis (2009) as 65% after 8 weeks of thermal degradation at 150 ^{o}C. In practice MEA thermal degradation in the presence of CO_2 at stripper temperatures is a slow phenomenon and that is why the temperature conditions chosen for the present study were higher than the thermal degradation studies presented in the literature by Davis and Rochelle (2008), Davies (2009) and Lepaumier et al. (2009a,b, 2010, 2011), in order to accelerate the degradation. Davis and Rochelle (2008), Davis (2009) and Lepaumier et al. (2009 a,b, 2010, 2011) state that 2-oxazolidone, N,N'-di(2-hydroxyethyl)urea, HEIA and HEEDA are the MEA major thermal degradation products. Some early studies performed on MEA thermal degradation pathways, presented 2-oxazolidone as the first MEA degradation product produced just by heating MEA carbamate (Polderman and Dillon, 1955). It was also suggest that HEIA was a precursor of HEEDA (Polderman and Dillon, 1955; Yavzikova et al., 1975). However, recent studies agree on the contrary: HEIA is thought to be the most stable degradation product and 2-oxazolidone to be the first and key product that causes the MEA deactivation (Davis, 2009; Lepaumier et al., 2009a,b, 2010, 2011; Vevelstad et al., 2011).

Fig. 1 presents the thermal degradation pathway as reported by Davis (2009), at many different parts of the proposed pathway, equilibrium reactions of the produced degradation products with CO_2 and MEA occur. Therefore, some of the thermal degradation products have also the capacity to remove CO_2.

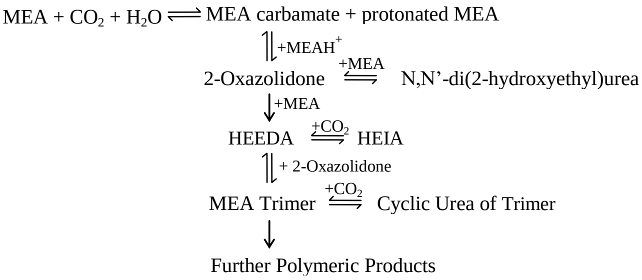

Fig. 1. MEA thermal degradation pathway in the presence of CO_2 as proposed by Davis (2009).

The present study focuses on the effects of thermal degradation on the MEA solvent. More specifically, the effects of thermal degradation on the MEA loss, the formation of degradation products and the CO_2 uptake capacity deterioration are discussed. Two sets of experiments with two different initial molar loadings, 0.19 and 0.37 mol of CO_2/mol of MEA, were performed in order to assess the effect of loading on the solvent operational lifetime.

2. Materials and methods

2.1. Experimental procedure

Fig. 2. Schematic of the absorption/stripping apparatus

A volume of 1200 ml of 30% (w/v) (or 29.6%, v/v) aqueous MEA (99.5%, Fisher Scientific) solution was contacted with pure CO_2 at a rate of 100 ml/min in the gas absorption/stripping rig (Fig. 2) until the desired loading was achieved (see Section 2.2). Two sets of experiments were performed in order to assess the effect of CO_2 concentration on thermal degradation. The target loadings for these sets of experiments were 0.19

and 0.37 mol of CO_2/mol of MEA and were determined by the inorganic carbon content measurement performed using a TOC (Total Organic Carbon) analyser (see Section 2.2). These loadings were not the 'ultimate' loading possible for MEA contacted with pure CO_2, but rather loadings chosen to be as close as possible to those used in other thermal degradation studies, which ranged from 0.20 to 0.40 (Davis and Rochelle, 2008; Davis, 2009; Lepaumier et al., 2009 a,b, 2010, 2011).

The samples were loaded into three high pressure vessels, from Parr Instrument Company Ltd., with maximum working pressure of 20 MPa, equipped with pressure gauges and were thermally treated in a forced convection oven at 160 ◦C for 2, 3 and 8 weeks. The thermal treatment temperature was chosen to be 160 ◦C, somewhat higher than those encountered in actual operating plants (120 ◦C), to produce highly degraded samples within a reasonable timescale. Note here that, according to Davies (2009) and Polderman and Dillon (1955), thermal degradation of MEA by carbamate polymerisation occurs at temperatures below 200 ◦C at the presence of CO_2. Davis and Rochelle (2008) and Lepaumier et al. (2009 a,b, 2010) report the same major degradation products for temperatures up to 150 ◦C and an increase in their production rates at higher temperatures.

After the end of the thermal treatment, the residual CO_2 was released from the samples until a specified CO_2 concentration was measured using a microGC instrument. The CO_2 left in the degraded solutions after the end of stripping was measured by means of the TOC instrument (see Section 2.3). The degraded samples were then analysed using GC–MS (see Section 2.4) to determine the MEA concentrations and identify thermal degradation products. Finally, in order to assess the effect of thermal degradation on the MEA CO_2 uptake capacity an absorption cycle was applied to the samples as described in Section 2.2. The absorption cycle was stopped when the CO_2 concentration at the absorption/stripping apparatus (Fig. 2) outlet approximately equalled the inlet. The number of moles of CO_2 absorbed by the samples was measured throughout the course of the absorption cycle by TOC measurements on aliquots drawn from the reactors (see Section 2.2). In the present study, the number of moles the degraded solutions could absorb, under the experimental conditions described, is termed as CO_2 uptake capacity and it should not be confused with the solvent's working capacity (number of mole of CO_2 removed/mole of circulated solvent, Veawab et al., 2001) under real plant conditions where CO_2 concentrations in flue gas are substantially lower.

2.2. Loading of CO_2 into MEA

The experimental procedure used to load samples of aqueous MEA with CO_2 is described below. This procedure was used to load the original MEA samples with CO_2 prior to thermal degradation and also to test the solvent's CO_2 uptake capacity after thermal treatment. The loading was performed in the absorption/stripping apparatus (shown in Fig. 2) and the procedure was as follows:

Absorption:
- The temperature in the oil bath was raised to 50 ◦C and the feed gas inlet valve was opened.
- 100 ml/min of pure CO_2 was bubbled into the reactor through a pre-saturator to maintain the water balance in the system.
- Any excess CO_2 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, aliquots of 0.1 ml were taken every 30 min and measured for their inorganic carbon content.
- These measurements were made with a Shimadzu Total Organic Carbon (TOC) Analyser TOC-500(A) using the TOC-control-V software. The instrument response was in mg C/L of solution which was used to calculate the moles of CO_2 in the solutions and the molar loading. This procedure was used in line with previous studies (Bishnoi, 2000; Chi, 2000; Freeman et al., 2010; Hilliard, 2008; Pacheco, 1998) where phosphoric acid can be used to acidify the CO_2 loaded amine samples to release aqueous CO_2, carbamate and bicarbonate as gaseous CO_2. After the absorption finished the feed gas valve was closed.

2.3. CO_2 removal – post thermal treatment

After completion of the prescribed thermal treatment, samples were taken from the high pressure vessels and loaded into the absorption/stripping apparatus (Fig. 2). The first objective was to release the CO_2 left in the samples. The stripping process conditions are as follows:

- The temperature in the oil bath was raised to 120 ◦C, the feed gas inlet valve was opened and 200 ml/min of pure N_2 were bubbled into the reactor to ensure good agitation.

- The outlet gas composition was measured with a portable microGC system throughout the stripping process. The system used was a Varian CP-4900 running Galaxie software (calibration gas 16% (v/v) O_2, 10% (v/v) CO_2 in a N_2 balance).

- The stripping process stopped when the CO_2 concentrations were below 0.2% (v/v), as determined by the microGC. The residual CO_2 still left in the solutions was measured using the Total Organic Carbon (TOC) Analyser as per Section 2.2. in order to assess the effect of degradation on the solvent's CO_2 uptake capacity.

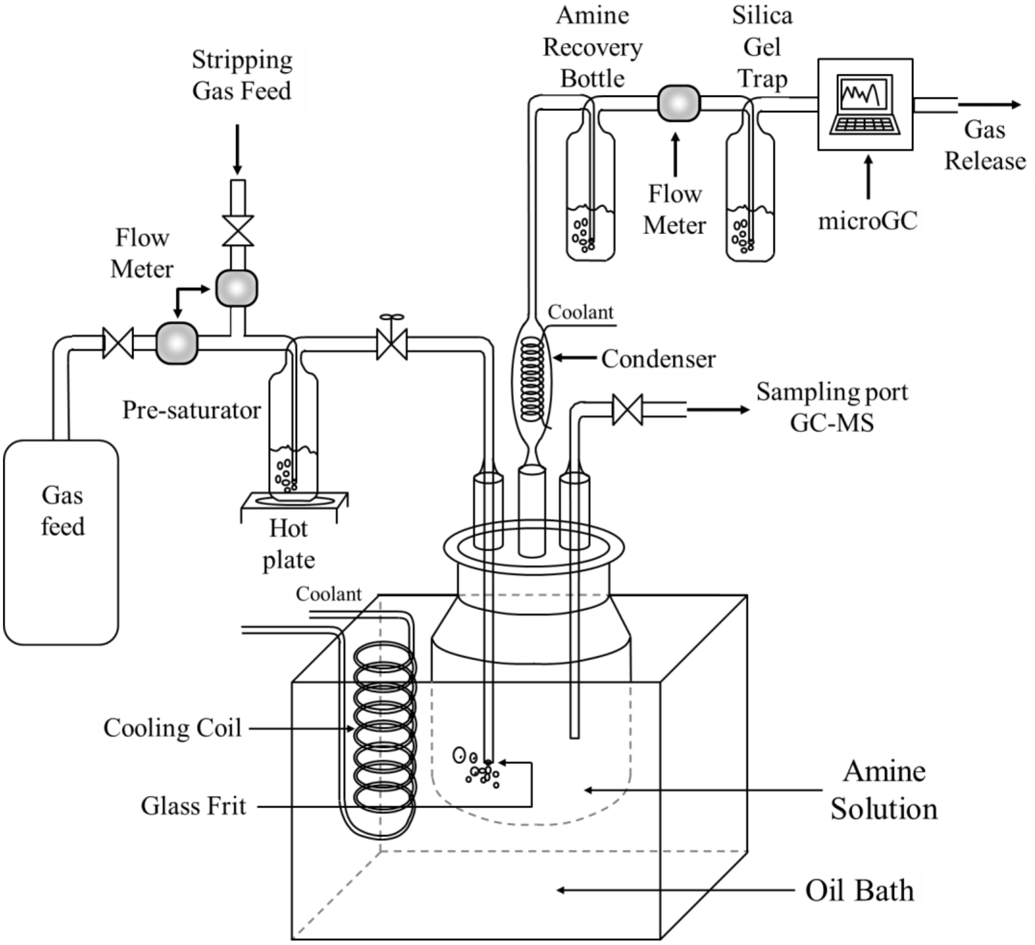

Fig. 2. Schematic of the absorption/stripping apparatus

After the removal of the CO_2 from the samples after thermal treatment the samples were again loaded with CO_2, as described in Section 2.2,

2.4. MEA and degradation product analysis by gas chromatography mass spectrometry

After the absorption experiments, the CO_2 absorbed by the degraded MEA samples was released and the samples analysed by means of gas chromatography mass spectrometry (GC–MS), to measure the amine losses and detect and quantify any degradation products generated during the process. The GC–MS system used was a Perkin Elmer CLARUS 500 GC–MS with the Rtx 5 Amine GC column purchased from Restek. The GC system experimental time was 14.50 min, the carrier gas (He) flow 50 ml/min, the initial oven temperature 50◦C and was held stable for 0.5 min and then raised up to 320◦C, with an increase rate of 20◦C/min, and remained stable for 0.5 min. The run time of the MS was 17 min and for the characteristic masses ranging from 10 to 200 m/z. Quantification was only performed for the MEA and its major thermal degradation products, HEIA (1-(2-hydroxyethyl)- 2-imidazolidone), HEEDA (N-(2-hydroxyethyl)-ethylenediamine) and 2-oxazolidone. The degradation products were identified in the EI (Electronic Impact) mode of the MS, using the MS spectra database available at the instrument software. For the quantification of the MEA and its major thermal degradation products in the samples, calibration curves were produced from commercially available standards.

2.5. CO_2 solubility experiment at 100◦C

As part of the design procedure for the sample thermal treatment system, it was deemed necessary to undertake the CO_2 solubility experiments in order to make sure it was safe to thermally treat the CO_2 loaded MEA samples at elevated temperatures for prolonged periods of time. The authors have included these data in the present section in the hope that is will be of assistance to other workers in the field that may be contemplating similar experiments. Samples of 400 ml of 30% (w/v) aqueous MEA solutions were loaded with pure CO_2 as described in Section 2.2. Thereafter, the initial CO_2 loading was determined and each sample was placed in the high pressure vessels. The vessels were sealed and placed in the oven at 100◦C until equilibrium was reached (it was assumed that equilibrium was reached when the pressure reading ofthe pressure gauge was stable for more than an hour). The total pressure was constantly measured and the CO_2 partial pressure was calculated using the method followed by Jou et al. (1995). The number of moles of CO_2 that were released by the MEA at this temperature, and moved to the headspace, was determined from the calculated CO_2 partial pressures. The CO_2 loading was then determined using the ideal gas law, in order to have a rough approximation (as CO_2 does not behave as an ideal gas) for more accurate results a correction factor should be used.

2.6. ICP-OES analysis for corrosion products

Liquid samples ofthe degraded MEA solutions with initial molar loading of 0.19 were analysed by the ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) for metals as corrosion of the high pressure vessels was suspected during the experiments. The metal losses per unit area and per unit area over time were calculated considering the vessel's surface area (282.6 cm^2) and the time as the degradation experiment duration, in days.

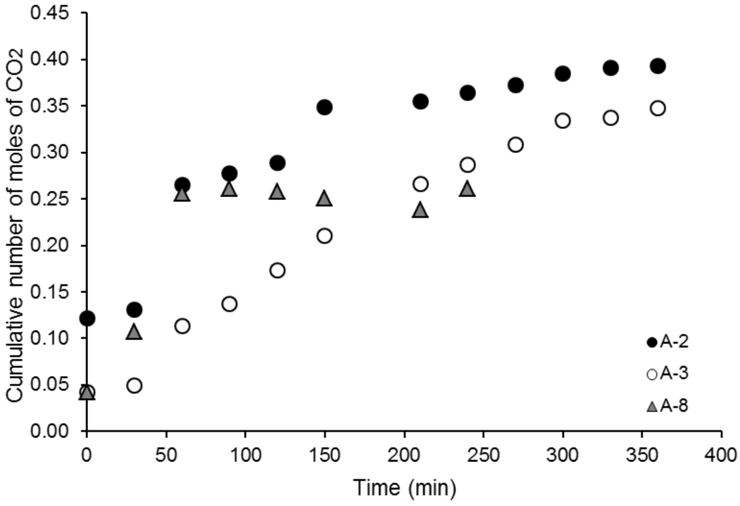

Fig. 3. Cumulative number of moles of CO_2 absorbed from the degraded samples with 0.19 initial molar loading

3. Results and discussion

3.1. Effect of degradation on MEA CO_2 uptake capacity

The three samples with initial molar loading of 0.19 mol of CO_2/mol of MEA were thermally treated at 160 ◦C at the high pressure vessels (referred to from here on as A-2, A-3 and A-8). The same procedure was followed to thermally treat the three samples with initial molar loading of 0.37 (referred to from here on as B2, B-3 and B-8). After thermal treatment the samples were tested in the absorption-stripping rig (Fig. 2) to assess the effect of degradation on the solvent's CO_2 uptake capacity, as described in Section 2.1. The CO_2 left in the degraded samples was released and they were then loaded with CO_2 in the absorption/stripping apparatus (Fig. 2). Inorganic carbon content measurements were used to assess the solvent's behaviour during absorption. Note here that during absorption under real plant conditions, the solvent is not in equilibrium with pure CO_2. The samples in this study are compared under the same experimental conditions.

Fig. 3 presents the number of mole of CO_2 absorbed by the samples that were thermally treated containing 0.19 mol of CO_2/mol of MEA. It must be noted here that some CO_2 remained in the degraded samples after the first stripping and these were determined using the TOC analyser as 0.12, 0.041 and 0.042 mol of CO_2 for the 2, 3 and 8 week degraded samples respectively. Fig. 4 presents the number of moles of CO_2 captured by the degraded samples over time for samples B-2, B-3 and B-8. Once again, the amounts of CO_2 that remained in solution after the first stripping, as determined by the TOC, were 0.1, 0.05 and 0.04 mol of CO2 for the 2, 3 and 8 weeks degraded samples, respectively. As expected, both the A-8 and B-8 samples absorb less CO_2 than the other samples that degraded for 2 and 3 weeks. From Fig. 3 it can be observed that A-8 absorbed 0.262 mol of CO_2. Considering that a pure MEA solution with 30% (w/v) initial concentration has the potential to absorb circa 0.98 mol of CO_2, it is concluded that the A-8 solution has lost approximately 74% of its ability to absorb the gas. Similarly, as presented in Fig. 4, the B-8 solution after 8 weeks of thermal treatment has lost approximately 77.2% of its ability to absorb the gas, a value slightly in excess of that found for A-8 (Fig. 3). Davis (2009) found that doubling the initial molar loading of CO_2 from 0.2 to 0.4 roughly doubles the initial degradation rate at 135◦C. In the present work, both in the 2 and 3 weeks samples, roughly 20% more MEA loss was observed in samples B-2 and B-3 samples when compared with the A-2 and A-3. The effect was not as prominent in the 8 weeks samples in both cases, as the samples were already highly degraded. It seems that the temperature increase (160 ◦C in the present study, instead of 135 ◦C) has a more dramatic effect on MEA loss than the initial CO_2 molar loading. Davis (2009) also suggests that an increase of 15◦C in the temperature quadruples the MEA loss.

3.2. Thermal degradation products identification and quantification

A number of degradation products were observed in the samples that were thermally treated with initial molar loading 0.19 and 0.37 mol of CO_2/mol of MEA. Based on the MS spectra database of the GC–MS, a list of compounds, identified at the present study that have also been previously reported in the literature, is presented in Table 1.

Apart from thermal degradation studies (Davis and Rochelle, 2008; Lepaumier et al., 2009 a,b), the compounds are also compared with pilot plant studies (Lepaumier et al., 2011; Strazisar et al., 2003) as well as laboratory scale studies performed at temperatures of up to 120 ◦C at the presence of both CO_2 and O_2 (Bello and Idem, 2005; Supap et al., 2006) as it was considered likely that some of those are thermal degradation products. Quantification was performed for the MEA, HEIA (1-(2-hydroxyethyl)-2-imidazolidone), HEEDA (N-(2- hydroxyethyl)-ethylenediamine) and 2-oxazolidone. Figs. 5 and 6 present the MEA, HEIA, HEEDA and 2-oxazolidone concentrations, as determined by the GC–MS, during the thermal treatment time for the samples with 0.19 and 0.37 initial molar loadings, respectively. N,N' -bis(2-hydroxyethyl) urea, a previously reported MEA thermal degradation product (Davis and Rochelle, 2008), was not detected in the samples during the present study. Lepaumier et al. (2011) also report that it was not possible to detect N,N' - bis(2-hydroxyethyl) urea at the samples analysed by GC–MS and indicate that this analytical method might not be appropriate for the detection of this type of compound.

As shown in Figs. 5 and 6, as the degradation experiment progresses, the MEA concentration decreases steadily from 30% (w/v) to 5.3 and 0.61% (w/v) in the A-8 and B-8, respectively. Moreover, at the beginning of the experiments the MEA concentration reduction was more dramatic than at the end of the thermal treatment. Of note are the very low final concentrations of MEA, showing degradations of the original amine in excess of 95% at 160◦C for the B-8 sample.

The integrated form of the rate equation was also plotted based on the MEA concentrations (as presented in Figs. 5 and 6), as determined by the GC–MS, in order to obtain an indicative kinetic plot, the order of the degradation reaction and an estimation of the rate constants based on four data points.

Table 1. Degradation products both detected in the thermally degraded samples with 0.19 and 0.37 initial molar loadings and previously reported in the literature

	A-2	A-3	A-8	B-2	B-3	B-8	Literature[1]						
Degradation Product							a	b	c	d	e	f	g
HEEDA	+	+	+	+	+	+	+	+	+				
HEIA	+	+	+	+	+	+	+	+	+	+	+		+
2-oxazolidone	+	+		+	+	+	+	+	+	+	+	+	
1-amino-2-propanol			+	+								+	
2-methylpiperazine			+									+	
2-methyl-3-oxazolidine		+	+	+								+	
4-methylmorpholine			+			+						+	
1-piperazineethanol			+			+						+	+
N-(2-hydroxyethyl)imidazole[2]	+	+	+		+	+					+	+	

[a](a) Davis and Rochelle (2008); (b) Lepaumier et al. (2009a); (c) Lepaumier et al. (2009b); (d) Strazisar et al. (2003); (e) Lepaumier et al. (2011); (f) Bello and Idem (2005); (g) Supap et al. (2006) and (a)–(c): lab scale thermal degradation studies; (d) and (e): degradation pilot plant samples; (f) and (g): lab scale degradation up to 120 ◦C with O2. b Commnly reported as oxidative degradation product

The degraded sample that was thermally treated with 0.19 initial molar loading was found to more closely fit 2nd order kinetics (R^2 = 0.9904) and the sample with 0.37 initial molar loading 1st order kinetics (R^2 = 0.9864) with respect to MEA. The calculated rate constants are 0.0201 $M^{-1}s^{-1}$ for the sample with 0.19 initial molar loading and 0.4779 s^{-1} for the sample with 0.37 initial molar loading.

Based on the afore mentioned calculations, it seems that the change in the CO_2 initial concentration possibly has an effect on the MEA thermal degradation pathway. This could be explained because according to Davis (2009), as shown in Fig. 1, at many different parts of the proposed pathway, equilibrium reactions of the produced degradation products with MEA or CO_2 occur. As a result, a change in the initial CO_2 concentration can favour different degradation reactions. As seen in Figs. 5 and 6, HEIA concentrations increased as the degradation time increased and it was determined as the major product in both samples A-8 and B-8. 2-Oxazolidone was detected both A-2 and B-2, but concentrations subsequently reduced over time, whereas HEEDA was almost stable for the first 3 weeks and then it slightly increased, in all samples. Lepaumier et al. (2009a,b) suggest that oxazolidones react very easily with another amine to give additional products; therefore, the absence of 2-oxazolidone from the 8 weeks samples is what would be expected, based on these previous studies. Figs. 7 and 8 present the percentages of each compound in the degraded solutions with 0.19 and 0.37 initial molar loading. respectively. These percentages were calculated by a nitrogen balance performed based on the concentrations of each compound in the final solutions, as determined by GC–MS. It needs to be noted here that for the purposes of the mass balance as 100% the nitrogen present in the initial MEA solution, is considered.

As can be seen from both Figs. 7 and 8, based on the nitrogen balance, HEIA accounts for a considerable amount of the MEA loss in the A-8 and B-8 degraded sample (55% and 76%, respectively). This indicates that HEIA is the most stable thermal degradation product. Clearly only three of the MEA thermal degradation products detected in the degraded samples were quantified.

Therefore, it was not possible to account for all the MEA loss. The total MEA loss was approximately 83% and 95%, for A-8 and B-8 degraded samples, respectively. HEEDA follows, accounting for 5% of the MEA loss but with no considerable changes in its concentration throughout the course of the experiment. This supports previous work by Davis and Rochelle (2008), Davis (2009) and Lepaumier et al. (2009 a,b, 2010, 2011) who suggest that HEEDA is an intermediate MEA thermal degradation product and it is HEIA's precursor. Of note are the very low final concentrations of MEA, indicating degradation of the MEA, initially in solution, of about 95% in 8 weeks at 160 ◦C for the B-8 sample. If it is supposed that only MEA has the capacity to uptake CO_2, then the absorption/stripping study suggested a somewhat lower degradation of the MEA, since the degraded solvent maintains a higher capacity of the solvent for CO_2. This observation is more prominent in the B-8 sample, which still retains 22% of its capacity to remove CO_2, although most of the MEA has been lost (95%), according to the GC–MS measurements. This, then, is an indication of the ability of some of the degradation products to absorb and release CO_2.

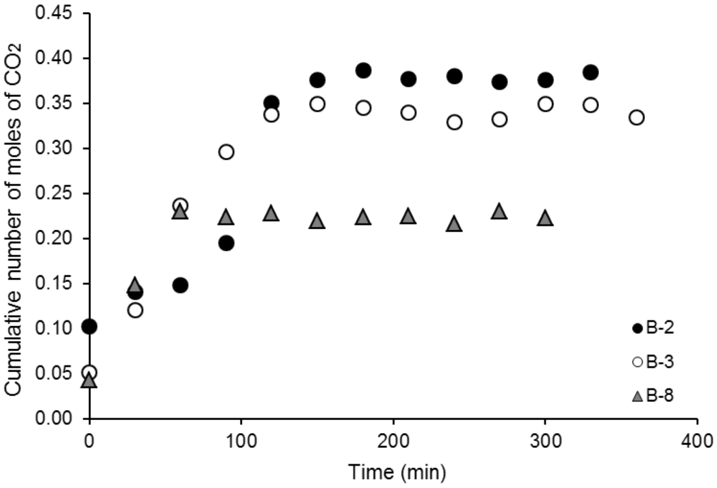

Fig. 4. Cumulative number of moles of CO_2 absorbed from the degraded samples with 0.37 initial molar loading.

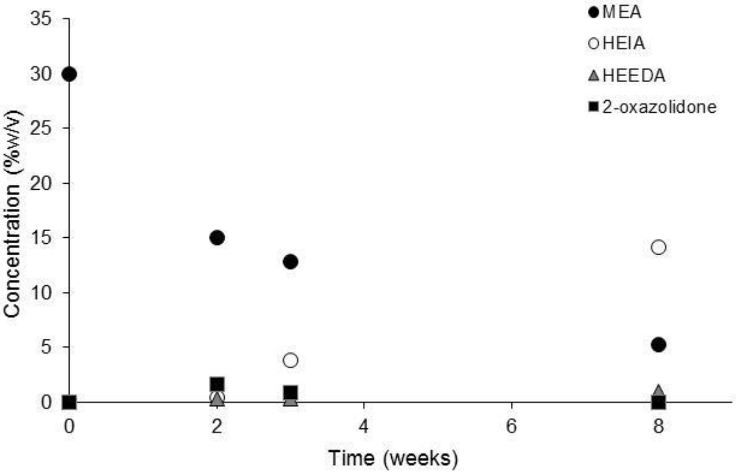

Fig. 5. MEA loss and HEIA, HEEDA and 2-oxazolidone formation during the thermal degradation experiments over time for the samples with 0.19 initial CO_2 loadings.

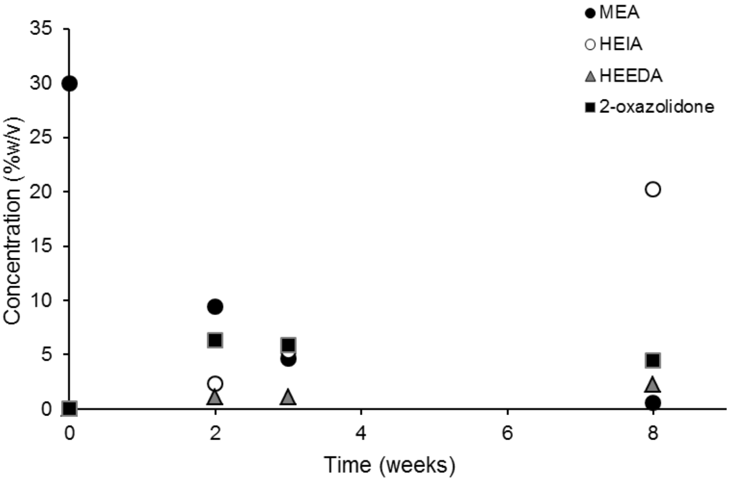

Fig. 6. MEA loss and HEIA, HEEDA and 2-oxazolidone formation during the thermal degradation experiments over time for the samples with 0.37 initial CO_2 loadings.

3.3. Comparison of degraded MEA behaviour as determined by GC–MS and CO_2 uptake capacity

A comparison can be made between the measured total number of moles of CO_2 absorbed by the degraded samples and the amount of pure CO_2 that the MEA present could theoretically remove (if considering the MEA as the only CO_2 absorbing agent present). Figs. 9 and 10 present the determined figures for the samples with 0.19 and 0.37 initial molar loadings, respectively. As shown in Fig. 10, very low final concentrations of MEA were determined, indicating degradation of the MEA, initially in solution, of about 95% in 8 weeks at 160◦C for the B-8 sample. As presented in both Figs. 9 and 10, the solvent demonstrated a CO_2 uptake capacity higher than that achievable by the MEA present. This observation is more prominent in the B-8 sample and it was calculated that the remaining solution still retains 22% of its capacity to remove CO_2, although most of the MEA has been lost (95%). This demonstrates the ability of some of the degradation products to absorb and release CO_2.

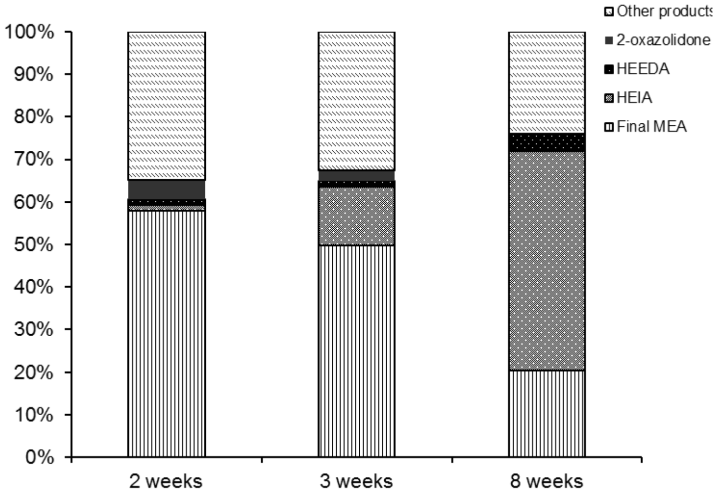

Fig. 7. Nitrogen balance in the degraded samples with 0.19 initial CO_2 loading

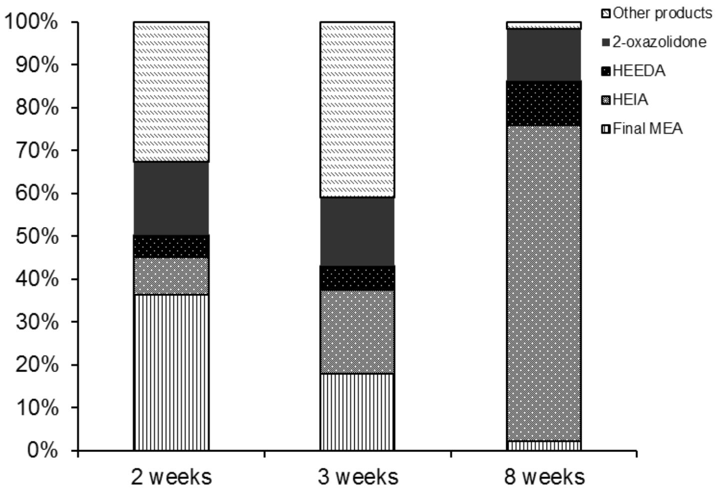

Fig. 8. Nitrogen balance in the degraded samples with 0.37 initial CO_2 loading.

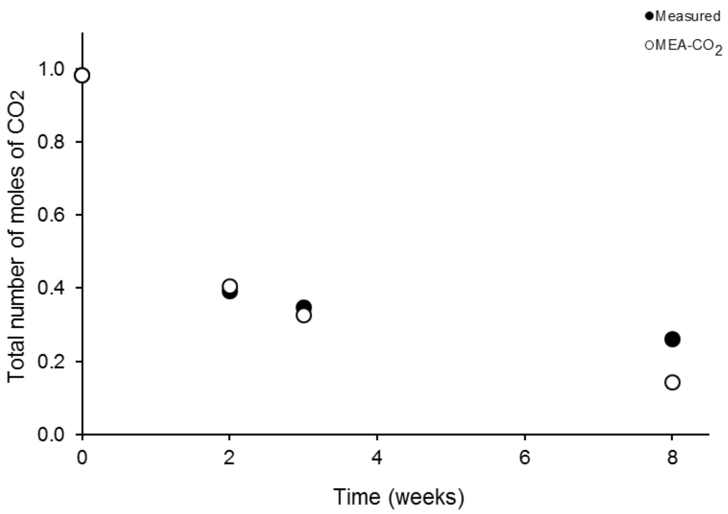

Fig. 9. Comparison of the measured CO_2 uptake capacity of the degraded samples with 0.19 initial molar loading compared to the calculated based on MEA content.

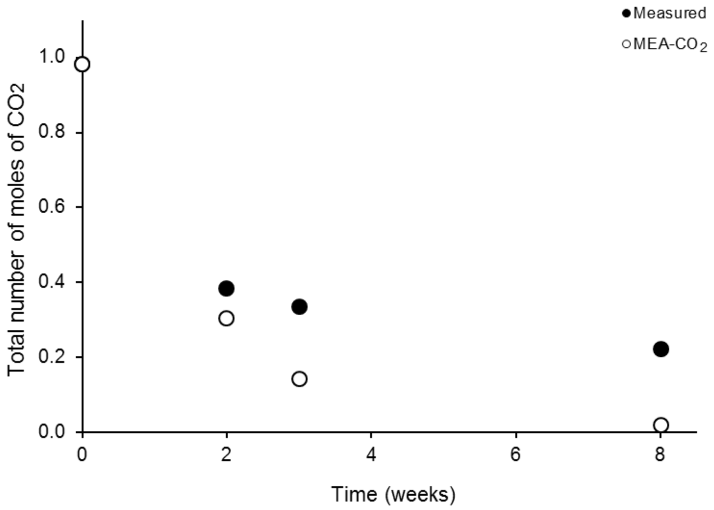

Fig. 10. Comparison of the measured CO_2 uptake capacity of the degraded samples with 0.37 initial molar loading compared to the calculated based on MEA content.

3.4. CO_2 solubility experiment at 100 ◦C

Table 2 presents the experimental data generated by the present study and also summarises CO_2 solubility data found in the literature. From the comparison of the results of the present experiment with the data shown in the literature (see Table 2), it can be concluded that the solubility data seem to differ between studies. In general the data produced by this set of experiments show higher CO_2 partial pressures than the literature. The values obtained by the study performed by Shen and Li (1992) seem to come in close agreement with the data from the present work at high CO_2 loadings. In all the literature studies presented the aqueous MEA solution volume was smaller than in this study, as well as the total system volumes.

3.5. Corrosion

The metal losses per unit area and per unit area over time of the degradation experiments were calculated (see Table 3), based on the liquid sample metal analysis and show that corrosion of steel occurs in the presence of CO_2 at elevated temperature and pressure. Whilst corrosion in actual plant will also be affected by the presence of O_2 and other gases, these data are included to provide indicative rates for the conditions presented. Table 4 presents the grade of steel of the vessels used in the present study. Noticing the major elements of the high pressure vessels provided by the manufacturer (Table 4) the highest metal percentages are those of Fe, Ni and then Cr. Thus, it seems that the vessels do not corrode uniformly. An overall corrosion rate of 1.95 mm/year was calculated based on the metal content of the solution determined in the B-8 sample (Table 3). It should be noted that Davis (2009) performed thermal degradation experiments; to test if thermal degradation can be catalysed, spiking up the MEA samples with metals such as Fe, Ni and Cr. According to the present study the thermal degradation rates were not affected by the presence of these metals.

Table 3 Corrosion rates of the high pressure vessels during the degradation experiments of MEA.

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

Table 4 Percentage of major elements of the high pressure vessels

Material	Fe (%)	Ni (%)	Cr (%)	Mo (%)	Mn (%)
T316 Stainless Steel	65	12	17	2.5	2.0

Table 2. CO_2 solubility data at 100 ◦C for different CO2 molar loadings.

Present Study		Shen & Li (1992)		Jou et al (1995)		Ma'mum et al (2005)	
Molar Loading	CO_2 Partial Pressure (kPa)	Molar Loading	CO_2 Partial Pressure (kPa)	Molar Loading	CO_2 Partial Pressure (kPa)	Molar Loading	CO_2 Partial Pressure (kPa)
0.039	60.1	0.227	2.8	0.0117	0.00724	0.155	7.354
0.225	96.3	0.279	8.5	0.0566	0.136	0.2326	19.62
0.283	371.9	0.305	19.9	0.188	1.43	0.2901	39.18
0.352	406.9	0.348	99.9	0.381	19	0.3594	92.79
0.414	441.9	0.427	379	0.422	39	0.38882	137.9
0.446	685.12	0.457	772	0.477	69	0.4182	191.9

4. Conclusions

As evidenced by the measured MEA concentrations and the measured CO_2 uptake capacity, despite having lost most of their MEA due to thermal degradation, the samples still retained some of their capacity to remove CO_2. This clearly indicates the ability of some of the degradation products to remove CO_2. Therefore, the requirement for MEA make-up may not be quite as serious as initially believed.

Observing the deterioration in the CO_2 absorbed by the degraded samples after 8 weeks of thermal treatment (82% A-8 and 95% B-8), it can be concluded that the initial molar CO_2-loading of the samples did not strongly influence the solvent degradation, in both cases the MEA has almost disappeared. The effect of the initial molar CO_2-loading was more considerable in the 2 and 3 weeks samples, where approximately 20% greater MEA loss was determined for the samples with 0.37 initial molar loading. In terms of the major MEA thermal degradation products, 2- oxazolidone, HEEDA and HEIA represent the vast majority of the species in solution after degradation based on the N balance. The MEA concentration loss is more dramatic at the beginning of the experiment, indicating that the rate of MEA degradation slows as the sample degrades more.

In both the A-8 and B-8 samples, HEIA concentration accounts for most of the MEA loss and appears to be the most stable degradation product based on the concentrations measured in both samples over time. The HEEDA and 2-oxazolidone concentrations had a less considerable change over time, which indicates that they are intermediate products to HEIA. Finally, corrosion of the thermal degradation rig was observed during the experiments with a calculated overall rate of 1.95 mm/year.

Acknowledgements

The authors greatly appreciate the support provided by Professor Keith Williams throughout this project. The authors would also like to thank the British Coal Utilisation Research Association (BCURA) for the funding provided for this research and Dr Michael Whitehouse (RWE npower) for his valued comments and discussions during this project.

References

Abdi, M.A., 1997. Purification of Partially Degraded Diethanolamine Solutions. University of British Columbia, Canada (PhD Thesis).

Bello, A., Idem, R.O., 2005. Pathways for the formation of products of the oxidative degradation of CO_2-loaded concentrated aqueous monoethanolamine solutions during CO_2 absorption from flue gases. Industrial and Engineering Chemistry Research 44, 945–969.

Bishnoi, S., 2000. Carbon Dioxide Absorption and Solution Equilibrium in Piperazine Activated Methyldiethanolamine. University of Texas at Austin (PhD Thesis).

Brakstad, O.G., Silva, E.F., Syversen, T., 2010. TCM Amine Project: Support on Input to Environmental Discharges, Evaluation to Degradation Components Version 3. Report No SINTEF F16202.

Chi, S., 2000.Oxidative Degeneration of Monoethanolamine. University of Texas at Austin (MS Thesis).

Davis, J., Rochelle, G.T., 2008. Thermal degradation of monoethanolamine at stripper conditions. In: 9th International Conference on Greenhouse Gas Control Technologies, Washington,

DC. Davis, J., 2009. Thermal degradation of Aqueous Amines Used for Carbon Dioxide Capture. University of Texas at Austin (PhD Thesis).

Eide-Haugmo, I., Lepaumier, H., Einbu, A., Vernstad, K., da Silva, E.F., Svendsen, H.F., 2011. Chemical stability and biodegradability of new solvents for CO2 capture. 10th International Conference on Greenhouse Gas Control Technologies. Energy Procedia 4, 1631–1636.

Freeman, S., Davis, J., Rochelle, G.T., 2010. Degradation of aqueous piperazine in carbon dioxide capture. 10th International Conference on Greenhouse Gas Control Technologies. Energy Procedia 4 (5), 756–761.

Hilliard, M., 2008. A Predictive Thermodynamic Model for an Aqueous Blend of Potassium Carbonate, Piperazine, and Monoethanolamine for Carbon Dioxide Capture from Flue Gas. University of Texas at Austin (PhD Thesis).

Islam, M.S., Yusoff, R., Ali, B.S., Islam, M.N., Chakrabarti, M.H., 2011. Degradation studies of amines and alkanolamines during sour gas treatment process. International Journal of the Physical Sciences 6 (25), 5877–5890.

Jou, F.-Y., Mather, A.E., Otto, F.D., 1995. The solubility of CO2 in a 30% mass percent monoethanolamine solution. Canadian Journal of Chemical Engineering 73, 140–147.

Lepaumier, H., Picq, D., Carrette, P.L., 2009a. Degradation study of new solvents for CO2 capture in post-combustion. 9th International Conference on Greenhouse Gas Control Technologies. Energy Procedia 1, 893–900.

Lepaumier, H., Picq, D., Carrette, P.L., 2009b. New amines for CO2 capture. I. Mechanisms of amine degradation in the presence of CO2. Industrial & Engineering Chemistry Research 48, 9061–9067.

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. Industrial & Engineering Chemistry Research 49, 4553–4560.

Lepaumier, H., da Silva, E.F., Einbu, A., Grimstvedt, A., Knudsen, J.N., Zahlsen, K., Svendsen, H.F., 2011. Comparison of MEA degradation in pilot-scale with labscale experiments. 10th International Conference on Greenhouse Gas Control Technologies. Energy Procedia 4, 1652–1659.

Ma'mum, S., Nilsen, R., Svendsen, H.F., 2005. Solubility of carbon dioxide in 30% Monoethanolamine and 50% methyldiethanolamine solutions. Journal of Chemical & Engineering Data 50, 630–634.

Mangalapally, H.P., Notz, R., Hoch, S., Asprion, N., Sieder, G., Garcia, H., Hasse, H., 2009. Pilot plant experimental studies of post combustion CO2 capture by reactive absorption with MEA and new solvents. 9th International Conference on Greenhouse Gas Control Technologies. Energy Procedia 1, 963–970.

Moser, P., Schmidt, S., Sieder, G., Garcia, H., Stoffregen, T., Stamatov, V., 2011. The post-combustion capture pilot plant Niederaussem – results of the first half of the testing programme. 10th International Conference on Greenhouse Gas Control Technologies. Energy Procedia 4, 1310–1316.

Nguyen, T., Hilliard, M., Rochelle, G., 2011. Volatility of aqueous amines in CO2 capture. 10th International Conference on Greenhouse Gas Control Technologies. Energy Procedia 4, 1624–1630.

Pacheco, M., 1998. Mass Transfer, Kinetics and Rate-Based Modelling of Reactive Absorption. University of Texas at Austin (PhD Thesis).

Polderman, L.D., Dillon, C.P., 1955. Why monoethanolamine solution breaks down in gas treating service. In: Proceeding of the Gas Conditioning Conference, pp. 49–56.

Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Meuleman, E., Ferons, P., 2012. Towards commercial scale postcombustion capture of CO2 with monoethanolamine solvent: key considerations for solvent management and environmental impacts. Environmental Science & Technology 46, 3643–3654.

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

Shen, K.P., Li, M.H., 1992. Solubility of carbon dioxide in aqueous mixtures of monoethanolamine with methyldiethanolamine. Journal of Chemical and Engineering Data 37, 96–100.

Strazisar, 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.

Veawab, A., Arronwilas, A., Chakma, A., Tontiwachwuthikul, P., 2001. Solvent formulation for CO2 separation from fluegas streams. In: First National Conference on Carbon Sequestration, Washington, DC.

Vevelstad, S.J., Eide-Haugmo, I., da Silva, E.F., Svendsen, H.F., 2011. Degradation of MEA; a theoretical study. 10th International Conference on Greenhouse Gas Control Technologies. Energy Procedia 4, 1608–1615.

Yavzikova, N.V., Zelenskaya, L.G., 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.