An Evaluation of Monoethanolamine (MEA) degradation and mitigation under the conditions used in submarine carbon dioxide removal plants

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Abstract

The current carbon dioxide (CO_2) removal system on Royal Navy (RN) submarines is based on the amine, monoethanolamine (MEA). This reversibly binds CO_2 under ambient conditions and releases it when heated. However, this amine degrades within the plant yielding hazardous compounds including ammonia (NH_3). In this study laboratory test apparatus was used to evaluate MEA solutions containing a range of inhibitor additives to determine which best suppressed degradation. A series of additional experiments were carried out to optimise the sorbent used to remove reaction adducts and metal impurities from the MEA within the system. These investigations concluded that the existing inhibitor additive was the most appropriate based on performance, cost, and exposure hazard but reduced rates of MEA degradation could be achieved by using alternative sorbent media. The kinetic methodology presented can also be applied to new CO_2 removal technologies including solid amines which also degrade and release NH_3.

1   Introduction

The RN has a duty of care to provide a safe environment for submariners and this includes maintaining a breathable atmosphere with contaminants kept as low as reasonably practicable (ALARP). A key requirement is a removal system that removes CO_2 produced by respiration of the personnel on-board and other activities such as food preparation. The current system achieves this using the reversible absorption and de-absorption of CO_2 from MEA. Like all amine based CO_2 removal technologies this relies on the formation of a stable carbamate. Although CO_2 levels are maintained within acceptable limits the breakdown of MEA within the removal plant results in some NH_3 release to the atmosphere. NH_3 is a hazard to health and its atmospheric concentration is monitored and controlled within action levels.

MEA degrades into organic decomposition products and NH_3. The rate of MEA degradation is dependent on several factors such as temperature, impurities present and CO_2 loading. Figure 1-1 shows the effect of CO_2 loading and temperature on the degradation of MEA that had been stored in a sealed steel container[i].
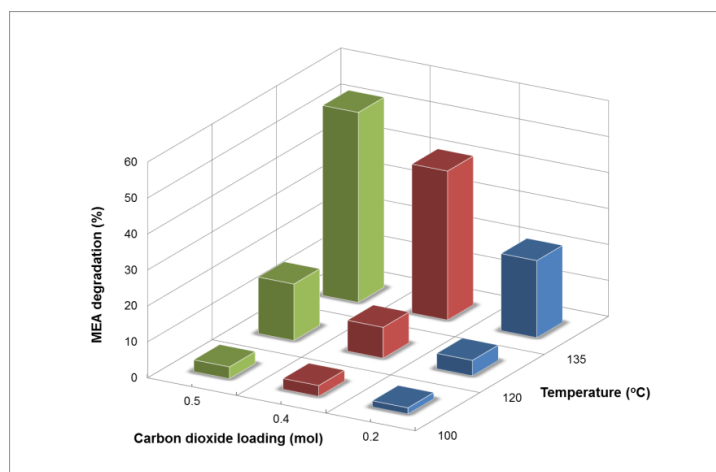
Figure 1-1: The effect of CO₂ loading and temperature on MEA degradation[i]

Previous work conducted by the Admiralty Research Establishment (ARE) suggested that MEA auto-oxidation occurred *via* two routes: air oxidation and irreversible condensation brought about *via* CO_2 adsorption. Numerous complex reaction pathways have been documented that indicate NH_3 can be produced from both the direct breakdown of MEA and the breakdown of other organic reaction products[i,ii,iii].

The use of deionised water to prepare low-ion MEA solution (LIMEA) and the addition of an inhibitor improves the stability of the MEA within the CO_2 removal plants. Additional stability is provided by a filtration systems that removes formed reaction adducts (by-products) from the MEA solution. Periodic replacement of the inhibited MEA solution will maintain as low a rate of MEA breakdown as possible.

MEA degradation is also promoted by metal impurities and formed peroxide species. These react with MEA to produce free radicals which then result in MEA decomposition to organic by-products and NH_3. Peroxides can be produced from organic and inorganic contamination of the LIMEA from the atmosphere. Metal impurities derive from corrosion of the steel used in the construction of the plant. Due to the elevated operating temperature of the CO_2 stripper, corrosion is greatest in this location. Inhibitor additives in the LIMEA mitigate the effect of impurities. Inhibitors suppress degradation by either chelation or reaction to produce non-reactive compounds. Inhibitors can also act as surface passivators which bind to the surface of the steel and retard corrosion.

Some MEA breakdown is inevitable and once formed organic by-products further accelerate the rate of decomposition. An activated charcoal filter is used within the CO_2 removal plant to remove these organic by-products. Alternative filter materials, such as zeolites and ion exchange resins, could remove more reactive by-products and reduce the rate of MEA breakdown.

The aim of the studies presented was to investigate the degradation of MEA under the conditions present within the CO_2 removal plant and assess the ability of both the existing and potential alternative inhibitor additives and filtration sorbents to reduce the rate of MEA breakdown.

2 Experimental

2.1 MEA degradation test apparatus

2.1.1 MEA degradation in the stripper only (static system)

LIMEA solution, either 250 ml or 500 ml of 30 w/w% MEA (4.5 M) was prepared and placed into either a 0.5 dm^3 round bottom flask or a 1 dm^3 flanged flask. The reaction vessel was fitted with a PEEK tubing which sparged the solution with air, a thermometer and a refluxing condenser. Test solutions were prepared using newly purchased MEA and deionised water. As required, pieces of 304 grade stainless steel (Advent Materials), with an exposed surface area of 8 cm^2 for 250 ml experiments or 16 cm^2 for 500 ml experiments, were added to the solution. The ammonia contaminated head-space of the sparged and heated reaction vessel flowed through gas-tight glassware to a round bottom flask containing an ion selective electrode (ISE) and acidified electrolyte (0.1 M copper sulfate and 0.1 M phosphoric acid). The ISE (ELIT 8051) measured the concentration of ammonium ion (NH_4^+) in solution using a NICO 2000 monitor (ELIT 9801), and a lithium acetate reference electrode (ELIT 003). The ISE was calibrated daily using prepared standards containing 1000, 100, 10, 1 and 0.1 ppm of ammonium chloride (NH_4Cl).

2.1.2 MEA degradation in a recirculating simulated CO_2 removal system

Recirculation of the solution allowed MEA filtration, CO_2 absorption and CO_2 de-absorption to occur simultaneously in separate sections of the apparatus (MEA flow shown as black arrows, Figure 2-1). Hot CO_2-lean MEA was extracted from the reaction vessel cooled to 60-80 °C using an external room temperature water bath (not shown), and transferred to the sorbent filter bed. A peristaltic pump circulated the MEA around the apparatus. MEA percolated through the filter and was collected in a dropping funnel. Either 0.5 or 1.0 % CO_2 was bubbled through the absorber at ~1 $dm^3.min^{-1}$. The MEA solution (now CO_2-rich) was returned to the reaction vessel at a rate of 10 - 20 $ml.min^{-1}$.
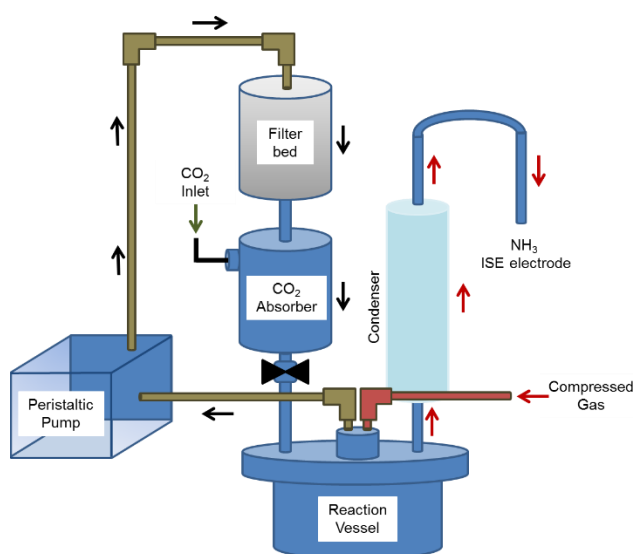

Figure 2-1: Schematic of the laboratory apparatus

2.2 Experimental method, data acquisition and interpretation

At the start of each experiment the ISE was calibrated and allowed to equilibrate for ~10 minutes in the electrolyte. Compressed air (~0.5 $dm^3.min^{-1}$) was used to sparge dissolved NH_3 from the reaction vessel for a further 10 min. In the static experiments, the MEA solution was heated at 5 ^{o}C.min^{-1} until the vapour above the solution reached 94 ±1 ^{o}C. In recirculating CO_2 removal experiments the peristaltic pump was operated until the reaction vessel contained 350 ml of MEA solution. The reaction vessel was then heated as above. The experiment was run at this temperature for a minimum of 5 h.

Throughout the experiment the ISE recorded the NH_3 concentration in the electrolyte every 10 s. The steady state degradation rate was taken as the average rate of NH_3 release after 10,000 s.

The rate of degradation of MEA is dependent upon the MEA concentration and can be approximated to:

$$Rate\ of\ degradation = k'[MEA]$$

The pseudo rate constant of degradation (k') includes all degradation pathways. Assuming a stoichiometric relationship between MEA breakdown and ammonia release the following equation can be used.

$$[MEA]_t = [MEA]_0 - [NH_3]_t$$

The concentration of MEA at time t ($[MEA]_t$) is given by the initial concentration MEA ($[MEA]_0$) and the emission of ammonia at time t, $[NH_3]_t$. The degradation rate constant k' was obtained from the gradient of a plot of $\ln([MEA]_0-[NH_3]_t)$ vs. time.

2.3 Inhibitor tests

Performance testing of seven inhibitor additives was carried out. Inhibitors were added to the prepared LIMEA solution prior to heating. All were purchased from Sigma-Aldrich and were analytical grade. The chemical functionality of each additive tested is shown in Table 2-1.

Inhibitor	Chemical functionality
1	Alcohol, carboxylic acid
2	Sulfoxide, amide, aromatic
3	Alcohol, pyridine-like
4	Pyridine-like, thioether
5	Azo, secondary amine, aromatic
6	Secondary amine, sulfoxide
7	Alcohol, ester

Table 2-1: Inhibitor functionality

2.4 Sorbent filter material tests

Seven commercially available sorbent materials were purchased and evaluated (Table 2-2). Each sorbent was weighed and made into a packed-bed retained by glass wool in a condensing tube. Sorbent 1, was the activated charcoal used currently in RN CO_2 removal plants and provided a baseline against which to compare the alternative materials.

The MEA test solutions contained either 20 mM or 200 mM of Inhibitor 1. The lower inhibitor concentration reduced MEA degradation suppression and enabled the relative effectiveness of the filter to be determined.

Sorbent	Description
Sorbent 1	Activated carbon (Granular)
Sorbent 2	Activated carbon (Pellet)
Sorbent 3	NH_3 enhanced functionalised activated carbon (Pellet)
Sorbent 4	Zeolite
Sorbent 5	Porous resin for cation & anion ion exchange
Sorbent 6	Cation ion exchange resin (strong)
Sorbent 7	Cation ion exchange resin (weak)

Table 2-2: Sorbent material functionality

3 Results & Discussion

3.1 MEA degradation – 250 ml sample

Initial experiments were conducted with 250 ml of LIMEA in a static system. The degradation of 4.5 M MEA without an inhibitor was determined as a baseline experiment. Degradation is likely to be Arrhenius dependant and therefore temperature would have an exponential effect on the reaction rate[iv]. Degradation of MEA primarily occurred at elevated temperature under CO_2 stripping conditions (> 100 °C).

Throughout the experiment NH_3 produced by MEA breakdown was captured by the acid scrubber in real-time. The acidified scrubbing solution protonates the NH_3 converting it to the ammonium ion, which was then measured by the ISE.
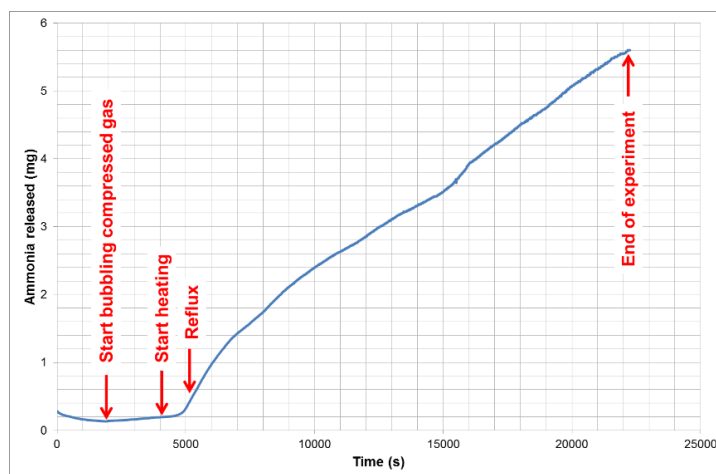

Figure 3-1: NH_3 release from 4.5 M MEA solution during an experiment

Figure 3-1 shows a typical plot of the NH_3 released during an experiment. At time = 0 s the apparatus was charged with the MEA solution and the ISE was switched on. The system was allowed to stabilise, then the bubbler was started. The introduction of compressed gas caused a small rise in the ISE reading as dissolved NH_3 from the auto-oxidation of MEA during storage volatised. The MEA solution was heated until the system was refluxing, causing an increase in release of NH_3. This experiment was repeated and the overall average rate of NH_3 release

was 3.47 x 10^{-4} mg.s^{-1}. This corresponds to a rate constant of degradation of 1.64 x 10^{-8} s^{-1} which was comparable with literature values (ca. 10^{-8}–10^{-6} s^{-1})[v].

3.2 Inhibitor additives

A range of degradation inhibitor additives were tested. These included aromatic compounds that are efficient radical quenchers and compounds with hydroxyl and amine functional groups which bond with metal surfaces and dissolved metal ions. The results of inhibitor evaluation experiments are shown in Figure 3-2 and Table 3-1. The best performing additives were Inhibitor 1 and Inhibitor 4 which had the lowest calculated rate constants of degradation ca. < 6.5 x 10^{-9} s^{-1}.
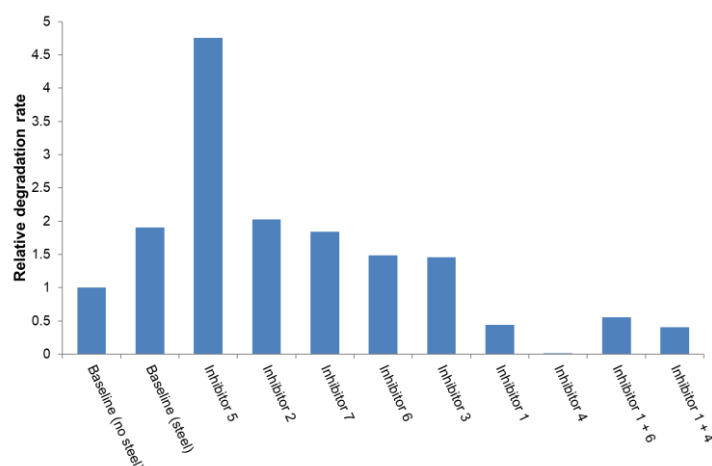

Figure 3-2: Relative degradation rates in the presence of steel and inhibitors

Experiment	Inhibitor	Test solution composition		k' (x10^{-8} s^{-1})
		MEA (M)	Inhibitor Concentration (mM)	
Test 1 – Baseline (no steel)	None		0	1.64
Test 2 – Baseline (steel)	None		0	3.85
Test 3	Inhibitor 5		200	7.76
Test 4	Inhibitor 2		200	3.42
Test 5	Inhibitor 7		200	2.95
Test 6	Inhibitor 6	4.5	200	2.51
Test 7	Inhibitor 3		100	2.48
Test 8	Inhibitor 1		200	0.65
Test 9	Inhibitor 4		100	0.02
Test 10	Inhibitor 1 + 6		200 (Inhibitor 1) 200 (Inhibitor 6)	0.89
Test 11	Inhibitor 1 + 4		200 (Inhibitor 1) 0.02 (Inhibitor 4)	0.61

Table 3-1: Inhibitor experiment test matrix

3.3   MEA with inhibitor additives degradation – 500 ml samples

Additional dynamic testing was carried out using larger volume samples (ca. 500 ml), containing Inhibitor 1 and Inhibitor 4. The results of these experiments are shown in the Table 3-2.

| Experiment | Inhibitor | Test solution composition | | k' $(\times 10^{-8}$ s$^{-1})$ |
		MEA (M)	Inhibitor Concentration (mM)	
Test 12	None		0	4.74
Test 13a			2	4.08
Test 13b	Inhibitor 1	4.5	20	2.15
Test 13c			200	0.13
Test 14a	Inhibitor 4		2	0.65
Test 14b			20	0.15

Table 3-2: Effect of Inhibitor 1 and Inhibitor 4 on MEA degradation rate constant (k')

In Test 12(no inhibitor) a degradation rate constant of 4.74×10^{-8} s^{-1} was found. In Tests 13a-13c the degradation rate constant decreased as the concentration of Inhibitor 1 was increased. The rate constant of degradation with 20 mM Inhibitor 4 (Test 14b) was comparable to that with 200 mM Inhibitor 1 (Test 13c), indicating Inhibitor 4 was approximately ten times more effective at reducing MEA degradation. Unfortunately exposure to Inhibitor 4 is more hazardous to health than exposure to Inhibitor 1.

3.4   The effect of CO_2

The effect of CO_2 on MEA breakdown rates was investigated in the absence of filtration or added steel pieces. In Test 15a, no CO_2 was introduced, Test 15c had an inlet CO_2 concentration of 0.5 % and Test 9 had a CO_2 concentration of 1.0 %. The results in Table 3-3 show a small decrease in k' as the inlet CO_2 concentration increased. Over the short duration of these tests the effect of CO_2 on degradation was not significant.

| Experiment | Test solution composition | | CO_2 (%) | k' $(\times 10^{-8}$ s$^{-1})$ |
	MEA (M)	Inhibitor 1 (mM)		
Test 15a			0	0.06
Test 15b	4.5	200	0.5	0.04
Test 15c			1.0	0.02

Table 3-3: Effect of CO_2 on the MEA degradation rate constant (k')

3.5   Effect of filter media on MEA degradation

3.5.1   Different amounts of Sorbent 1 and Inhibitor 1

Experiments were carried out with both CO_2 and steel pieces (ca. 16 cm^2) present in the recirculation system. Test 16a (without filtration) had a k' of 0.96×10^{-8} s^{-1} and this increased to 1.01×10^{-8} s^{-1} in Test 16b when 0.5 % CO_2 was bubbled into the absorber. Both degradation rates were more than ten times greater than in equivalent experiments not containing steel pieces. Tests 16c-16f were carried out using increasing amounts of Sorbent 1 (0.2-10 g), with Test 16f using the MEA used in previous tests therefore showing the increase in degradation

with aged MEA. During these experiments filtration of the MEA solution had no beneficial impact on degradation rates which increased from 3.16 to 6.55 x 10^{-8} s^{-1}.

Experiment	Test solution composition		CO_2 (%)	Sorbent 1 (g)	k' (x 10^{-8} s^{-1})
	MEA (M)	Inhibitor 1 (mM)			
Test 16a	4.5	200	0	0	0.96
Test 16b			0.5	0	1.01
Test 16c			0.5	0.2	3.16
Test 16d			0.5	2	4.31
Test 16e			0.5	10	6.55
Test 16f			0.5	0	6.67

Table 3-4: Effect of carbon filter

3.5.2   Sorbent 1 and Inhibitor 4

During recirculation experiments with Inhibitor 4 this additive precipitated in the colder parts of the test apparatus, *i.e.* the peristaltic pump and sorbent filter, causing flow problems. A sulfurous odour also was produced during this experiment which could indicate breakdown of the inhibitor. Due to these difficulties and the greater toxicity of this additive it is not considered suitable for use in submarine CO_2 removal plants.

3.5.3   Sorbent screening experiments using MEA containing Inhibitor 1

Several filtration sorbents were tested, Table 3-5 shows the experimental conditions used and the calculated MEA degradation rate constants (k'). Apart from Sorbent 2 and Sorbent 3 all sorbents had a lower k' than Sorbent 1 with 20 mM of Inhibitor 1. During Test 22 flow problems were encountered as the polymer sorbent expanded upon contact with the MEA solution. This experiment was repeated using less mass of Sorbent 7 to mitigate this problem. However at the end of this experiment the MEA solution had become turbid probably due to resin dissolution.

At 200 mM Inhibitor 1 experiments; Sorbent 2, Sorbent 5 and Sorbent 6 suppressed degradation and gave rise to lower k' than Sorbent 1. Sorbent 6 was the best at suppressing degradation with a measured rate constant of degradation of 4.2 x 10^{-9} s^{-1} (Test 22b).

| Experiment | Test solution composition | | Filter bed | | k' $\times 10^{-8}$ (s^{-1}) |
	MEA (M)	Inhibitor 1 (mM)	Sorbent	Mass (g)	
Test 17	4.5	20	-	-	0.89
Test 18a		20	Sorbent 1	10	1.23
Test 18b		200			1.16
Test 19a		20	Sorbent 2		2.51
Test 19b		200			0.91
Test 20a		20	Sorbent 3		2.15
Test 20b		200			1.52
Test 21a		20	Sorbent 5		0.60
Test 21b		200			0.74
Test 22a		20	Sorbent 6		1.15
Test 22b		200			0.42
Test 23a		20	Sorbent 7		0.78
Test 23b		20		2	1.35

Table 3-5: Single sorbent tests

Additional experiments were undertaken using combinations of activated charcoal and a second sorbent. The purpose of these experiments was to determine whether it was possible to achieve a synergistic effect with two materials. Carbonaceous adsorbents predominantly adsorb organic compounds, ion exchange resins mainly retain ionic species and zeolites are general adsorbents. Each experiment was carried out with Inhibitor 1, CO_2 and steel present. Dual adsorbent filter beds contained Sorbent 2 plus either Sorbent 5, Sorbent 6, Sorbent 7 or Sorbent 4. Due to its pelletised physical form, Sorbent 2 packed inefficiently creating voids that were filled with the second sorbent. This was particularly advantageous for Sorbent 7 which swelled and Sorbent 4 which was prone to caking. Table 3-6 gives the degradation rate constants for each of the five dual adsorbent filter beds tested.

| Experiment | Test solution composition | | Filter bed | | k' ($\times 10^{-8}$ s^{-1}) |
	MEA (M)	Inhibitor 1 (mM)	Sorbents	Mass (g)	
Test 24a	4.5	20	Sorbent 2 |Sorbent 5	5 | 5	1.88
Test 24b		200			4.78
Test 25a	4.5	20	Sorbent 2 |Sorbent 5	10 | 10	3.23
Test 25b		200			2.04
Test 26a	4.5	20	Sorbent 2 |Sorbent 6	5 | 5	3.50
Test 26b		200			0.45
Test 27a	4.5	20	Sorbent 2 |Sorbent 7	5 | 2	1.41
Test27b		200			0.27
Test 28a	4.5	20	Sorbent 2 |Sorbent 4	5 | 2	1.91
Test 28b		200			0.52

Table 3-6: Dual-bed sorbent tests

The worst performing dual adsorbent filter was sorbent 2 | sorbent 5 with a maximum degradation of 4.78 x 10^{-8} s^{-1} in test 24b. With 20 mM of Inhibitor 1 all dual adsorbent beds had greater degradation than Sorbent 1 alone. However, with 200 mM of Inhibitor, Sorbent 2 |Sorbent 6, Sorbent 2 |Sorbent 7 and Sorbent 2 |Sorbent 4 suppressed degradation and performed better than Sorbent 1 alone. The best sorbent filter was Sorbent 2 |Sorbent 7 which suppressed the degradation of MEA to 2.7 x 10^{-9} s^{-1} (Test 27b).

4   Conclusions

Investigations found that the currently used additive, Inhibitor 1, was the most appropriate of those tested when both performance and toxicity were considered. Some alternative sorbents outperformed the current used sorbent (sorbent 1) in a single-bed system. A dual-bed MEA filter containing two complimentary functionalities and forms, *i.e.* activated charcoal and ion exchange resin, had the lowest degradation rates measured.

Degradation of MEA was found to be dependent on all factors investigated. The concentration of the inhibitor additive had the greatest impact on MEA degradation with the sorbent filter media and CO_2 presence having an approximately equal but lesser effect.

Future investigations will focus on alternative dual-bed filters and identifying factors that affect longer-term degradation rates.

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