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METHOD DEVELOPMENT FOR PERFORMANCE TESTING OF CARBON CAPTURE SOLVENTS USING MONOETHANOLAMINE (MEA) AS A BENCHMARK SOLVENT UNDER POST-COMBUSTION CAPTURE CONDITIONS

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Method development for performance testing of carbon capture solvents using monoethanolamine (MEA) as a benchmark solvent under post-combustion capture conditions

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GLOSSARY/ABBREVIATIONS

AMP	2-amino-2-methyl-1-propanol
CCUS	Carbon capture utilisation and storage
DEA	Diethanolamine
DI	Deionised Water
DSIT	Department of Science, Innovation and Technology
DTPA	Diethylenetriamine penta(acetic acid)
EI	Electron impact
FT-IR	Fourier-transform infrared spectroscopy
GC-MS	Gas chromatography-mass spectrometer
HEDP	Hydroxyethylidene phosphonic acid
HEEDA	N-(2-hydroxyethyl)ethylenediamine
HTCS	High temperature cycling system
ISDA	Integrated solvent degradation apparatus
MEA	Monoethanolamine
MTF	Materials testing facility
NPL	National Physical Laboratory
PLC	Programmable Logic Controller
PRM	Primary Reference Material
PZ	Piperazine
R_s	Response factor
SEM	Secondary electron multiplier
TEA	Triethanolamine

EXECUTIVE SUMMARY

The work reported here was funded by NMS CCUS Net-Zero Uplift project funded by Department of Science, Innovation and Technology (DSIT). Under this project, a traceable method for performance testing of carbon capture solvents, by using MEA as a benchmark solvent, under post-combustion capture conditions was developed using the Materials Testing Facility (MTF) commissioned at NPL. MTF consisted of a high-pressure reactor combined with a continuous online monitoring system that recorded data from a mass spectrometer. Carbonation efficiency of MEA was tested by varying two experimental parameters, namely the amount of the capture solvent and the CO_2 amount fraction of the primary reference gas mixture used for the carbonation experiment. CO_2 uptake by MEA under the industrial flue gas condition using NPL PRM (containing 15 cmol/mol of CO_2 in N_2) varied between 0.40 – 0.42 moles CO_2 per mole of MEA. The measurement model reported an expanded uncertainty of 14.48% with a confidence level of 95% ($k = 2$). These preliminary results are in good agreement with the literature reports involving experiments under similar conditions. This validated the right functioning of the MTF at NPL for carrying out CO_2 capture performance evaluation of various industrially relevant carbon capture solvents under different experimental conditions. The method developed here using MEA as the benchmark capture solvent and NPL PRMs, can be used to compare the carbonation efficiency of other industrially relevant amine solvents. The developed method directly validates the efficacy of different capture technologies. It will also give useful insights on capture efficiency of different solvents helping technology developers to improvise on their capture materials. The system can also be used to study capture other important solvent characteristics such as, stability, cyclability over a period of time and accelerated aging experiments that identifies, quantifies and monitors any degradation products that evolve from the CO_2 capture solvent. Future work and impact that this work can have on the UK government, the UK industries, regulatory bodies by ensuring safe, effective and sustainable deployment of CCUS technology has been discussed.

1 INTRODUCTION

Carbon capture utilisation and storage is a key element in the arsenal of UK strategies for transitioning to a green economy and the overall target of meeting 'Net Zero' by 2050[1,2]. To provide a rapid, low-cost, safe, and reliable method of capturing carbon dioxide from various industrial processes, solid and liquid materials can be used[2]. The challenges to achieve this include accurate measurement of the capture capacity, sorbent homogeneity, sorbent stability, activity decay, repeatability, emissions/degradation products that can arise due to the capture technology and an absence of a standardised and traceable measurement platform to access various post combustion capture technologies. Therefore, there is a need to develop a metrology infrastructure using reference materials to validate various capture technologies that are being developed simultaneously to tackle climate change. The measurement infrastructure will also help and support the development of new sustainable capture technologies by giving feedback leading to modifications and improvement in process/technology. The arising results can be feedback to funding agencies to ascertain which technologies should be promoted. Traceable methods are also essential to assess the quality of the emissions coming from the CCUS technology which helps in identification and quantification of any harmful degeneration product given out in the process. Analysis and control of degeneration products emitted by CCUS technologies can help in framing and implementation of regulations regarding the air quality to safeguard the environment.

NPL was supported by the NMS CCUS Net-Zero Uplift project funded by Department of Science, Innovation and Technology (DSIT) to develop a traceable method for measuring the carbon dioxide capture capacity (*i.e.*, how much CO_2 can be absorbed by the material) involving NPL's primary reference materials, the results of which can be used for benchmarking and comparing various CCUS technologies evolving in the market. The NPL's material testing facility was developed by coupling a compact high-pressure Parr reactor with an online monitoring system that recorded data from a mass spectrometer. The flow of the gases and the data was recorded with the help of bespoke software providing a real-time reading of the concentration of the components in a gas mixture.

The following section of this report outlines the use of MEA as a carbon capture solvent, detailing its mechanism and conditions of use, as well as comparing it to other amine-based solvents. Following this, a discussion of the MEA sorption experiment results (and calculated uncertainties) using the materials testing facility at NPL is provided, with concluding remarks on future work and applications.

1.1 MECHANISM OF ABSORPTION

Industrially, several amine-based solvents are used to capture CO_2 but for method development at NPL, MEA, which has been widely used for CCUS applications has been used as a benchmark capture solvent. MEA shows a high absorption capacity for CO_2,[1] is inexpensive in comparison to other solvents[2] and produces water-soluble compounds as products on carbonation[3,4] (*i.e.*, carbamates).

The first step of capture is the chemical absorption of CO_2 in MEA, with the mechanism given as follows[5,6]. This involves the protonation of water and the hydrolysis of carbon dioxide to give carbonic acid.

$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$

$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons HCO_3^-{}_{(aq)} + H^+_{(aq)}$

This is followed by the protonation of the MEA and capture of the carbon dioxide molecule to form a carbamate, which is soluble in water. The reactivity therefore lies in the amine part of the Monoethanolamine (which can also be described as an alkanolamine).

$R\text{-}NH_{2(aq)} + H^+_{(aq)} \rightarrow R\text{-}NH_3{}^+_{(aq)}$

$R\text{-}NH_{2(aq)} + CO_{2(aq)} \rightarrow R\text{-}NHCOO^-_{(aq)} + H^+_{(aq)}$

Where, R= C_2H_4OH

MEA, following absorption, can be recycled, and thus regenerated for future use, and this reflects the regeneration step. This is an energy-intensive step[7] but can be catalysed[8] to reduce its thermodynamic demands.

1.2 TYPICAL CONDITIONS AND USE OF MEA

MEA has been used under a variety of capture conditions to identify and assess its most optimal capture efficiency. It is used in post-combustion capture conditions, where CO_2 is removed from the flue gas created after combustion[1]. Akram et al.[9] reported using a benchmark of 30 wt.% MEA at 30 °C and analysed the increase in wt. %, by increasing the wt. % to 40% and studied its effects at the National Core Facility. The effect of such an increase was intended to decrease the regeneration energy cost of MEA. This was measured using Fourier-Transform Infrared Spectroscopy (FT-IR), using the Gasmet DX 4000 analyser[10]. A flow rate of 40-50 L min^{-1} was used (reflective of the scale of the plant) and the sampled gas was analysed every 7 seconds. The principle behind FT-IR is identifying the infrared spectral profile of the gas and assessing changes in amount fractions based on the infrared absorption capacity of the gas[10]. The temperature, pressure and flow rate were collected from the FT-IR, Programmable Logic Controller (PLC) and Labview software logs.

The results agreed with the literature, with a capture efficiency of 89.6% for the increased solvent concentration of 40 wt.% with a 6.6 vol.% CO_2 gas stream. An increased temperature (from 125.7 to 126.8 ˚C) increases capture efficiency to 91%. MEA has also been used in other conditions. One study by Brigman et. al[11], outlines results from 30 wt. % and 40 wt. % aqueous MEA testing at the CO_2 Technology Centre Mongstad. The total mass recovery of CO_2, *i.e.*, the mass of CO_2 that was absorbed by MEA, was close to 100% of the total capacity of MEA for the two concentrations. The concentration was changed in a dynamic fashion, *i.e.*, maintained at 30 wt.% and then increased to 40 wt.%. This reflects the high absorption capacity of MEA as seen in other studies.

Although, there are a variety of conditions and concentrations of MEA used in the sorption experiments at industries and laboratories, the most commonly used conditions were selected to carryout preliminary experiments at NPL. Method development at NPL therefore used 3 and 5M MEA in water to study the effect of concentration on carbon capture efficiency.

1.3 DEGRADATION OF MEA AND THE USE OF ACCELERATED AGEING

As part of the mechanism, MEA can undergo degradation and secondary reactions to produce N-nitrosamines and nitramines[12-14], which are carcinogenic[15-17]. Degradation occurs via the polymerisation of carbamates[12] which are produced as part of the mechanism, which can then produce a variety of products, including 2-oxazolidinone, N-(2-hydroxyethyl) imidazolidinone, and N-(2-hydroxyethyl) ethylenediamine (HEEDA)[18]. When exposed to oxygen, further products include ammonia and low molecular weight organic acids[19]. These degradation products could be potentially corrosive to plant pipelines and thus a measurement method to quantify such degradation products is necessary, in terms of both safety and cost.

To further study the effect of degradation, 'accelerated ageing' may be used, whereby MEA is deliberately exposed to harsh environmental conditions to force a faster degradation, which can be studied and thus accounted for in typical CO_2 capture conditions[20]. A study by LaFrate et. al used MEA as a benchmark sorbent and compared it to ionic liquids for use in CCUS applications and applied accelerated ageing conditions[20]. The experiments were conducted with 30 wt. % aqueous MEA at 120 °C in sealed cylinders under nitrogen (N_2) and air. It was reported that the degradation was negligible with nitrogen and was slightly more present with air. The degradation products were identified using GC-MS (gas chromatography-mass spectrometry). When MEA was exposed to CO_2, emulating that of typical degradation conditions of 120 °C over 1 day, a significantly greater degradation presence was observed – with the study reporting hydroxylamine and ammonia after this time. Following this, however, no further degradation was observed until after three weeks, at which point carbamate polymerization was observed, which agrees with the mechanism proposed and products identified in other studies[9].

To summarise, the carcinogenic degradation products of 2-oxazolidinone, N-(2-hydroxyethyl) imidazolidinone, and N-(2-hydroxyethyl) ethylenediamine (HEEDA) are produced from the polymerisation of carbamates following absorption of CO_2 by MEA. When exposed to oxygen, ammonia and low molecular weight organic acids are produced. These are important compounds to analyse using the testing facility developed at NPL.

1.4 CYCLING

Multiple absorption-regeneration processes can be coupled, and this coupling is described as 'cycling'[21]. A study by Voice et. al[21] reports the use of various amines in CCUS, alongside MEA, and studies their degradation through a cycling process. Firstly, an integrated solvent degradation apparatus (ISDA) was used to flow 2 % CO_2 in oxygen into an oxidative reactor containing the solvent (MEA was at a concentration of 7M) thus stimulating oxidative degradation. This was followed by a high-temperature cycling system (HTCS), whereby the solvents were fed through to a heater, and then cycled back into the reactor. A mixture containing 12% CO_2 in air acted as the gas to be absorbed by the cycled solvents and was flowed in a 'mini plant' CO_2 capture system, which was at 120 °C and a pressure of 2.1 bar. Finally, the gas leaving the system was analysed by FT-IR. Degradation was quantified by the production of formate, which is a common oxidative degradation product, being one of the low molecular weight organic acids[19]. MEA showed considerable oxidative degradation after multiple cycles. However, when chelating agents hydroxyethylidene phosphonic acid (HEDP) and diethylenetriamine penta(acetic acid) (DTPA) were added, this reduced but did not eliminate oxidation in 7M MEA.

In summary, cycling is an important condition to consider. Typically using MEA with gas mixtures of 10-15% CO_2 and heated, coupled with the formation of degradation products, is a factor that can be analysed using the materials testing facility at NPL. Although in reality, MEA should have undergone several thousands of carbonation-decarbonation cycles to give rise to significant amounts of harmful degeneration products, an accelerated testing protocol to monitor the degeneration products can be developed to reduce testing time but generates the same results as expected from high number of carbonation-decarbonation cycles.

1.5 CATALYSTS FOR THE REGENERATION OF MEA

Other conditions, for example, include the use of catalysts[22], to increase the rate of CO_2 capture. Heterogeneous catalysis using nanoparticles is a common method of increasing the rate of regeneration of CO_2 capture solvents, including MEA. Catalysts include transition metal oxides such as TiO_2 and metal-organic frameworks such as Fe_3O_4-COOH nanoparticles[8,23]. In particular, the Fe_3O_4-COOH nanoclusters are water-dispersible. The catalytic activity of the nanoclusters was investigated with CO_2-rich MEA (5M) at 88 °C. The addition of 0.1 wt.%

Fe_3O_4–COOH significantly increased the kinetics of CO_2 desorption and resulted in ~27.3% less energy consumption, compared to that of a blank MEA solution.

It can thus be shown that a wide variety of catalysts are used to increase the rate of CO_2 capture, and therefore studying MEA solutions with a selected few catalysts can be planned for future experiments at NPL.

1.6 COMPARISON OF MEA WITH OTHER AMINE-BASED SOLVENTS

A variety of other amine-based solvents are used alongside MEA. These solvents can provide advantages over MEA for CCUS, particularly in lowering the energy cost of regeneration. A study by Kim et. al[24] investigated the absorption enthalpy of various amine-based solvents – these included MEA, diethanolamine (DEA), triethanolamine (TEA), and 2-amino-2-methyl-1-propanol (AMP). 30% CO_2 in N_2, fixed at a constant flow rate with an MFC, flowed through the solvents, at 100 g and 30% wt. concentration. The enthalpies were measured using a differential reaction calorimeter (DRC). The enthalpies of absorption were -88.91, -70.44, -44.72, and -63.95 kJ mol^{-1} respectively (at 298 K). These values appear to agree with the high energy cost associated with the desorption of CO_2 from MEA, as its absorption enthalpy is the most exothermic of the listed amine-based solutions, implying a highly endothermic desorption. The CO_2 absorption capacities were also measured, with the experiments conducted across a temperature range of 313 to 353 K at atmospheric pressure (1 atmosphere), flowing 30% CO_2 in N_2. CO_2 absorption was calculated by the difference between the concentration of inlet and outlet CO_2, which was measured by gas chromatography (GC). Table 1 illustrates the advantages and disadvantages of commonly used amine-based solvents for CCUS.

Table 1. Advantages, and disadvantages of amine-based solvents for CCUS. Reproduced from ref. 25.

Solvent	Advantages	Disadvantages
MEA	Fast absorption rate, high absorption capacity, high desorption efficiency	Slow desorption rate, high energy cost with desorption, carcinogenic side products
DEA	Reduced solvent loss due to byproduct formation[26]	The rate of absorption is slower compared to MEA[26]
MDEA	Long duration of absorption, high absorption capacity, low solvent consumption during absorption[27]	Slow absorption rate[27]
TEA	Cheap, low energy cost with absorption[26]	The rate of absorption is slower compared to MEA[26]
AMP	High absorption capacity, low regeneration energy cost[26]	Expensive, large solvent loss from evaporation[26]
Piperazine (PZ)	High absorption capacity, high yield of carbamates during CO_2 absorption[28]	A limited range of concentrations can be used[28]

1.7 MEASUREMENT METHODS USED

As was previously discussed, the interactions of CO_2 by MEA and other amine-based solvents are measured in a variety of ways, such as gravimetry, FT-IR and gas chromatographic analysis. Hiden Analytical partial pressure gas analysers[29,30] combined with mass spectrometers provide a new way of measuring these interactions. The advantages of these instruments, which are in use at NPL, include continuous analysis of gases and vapours at pressures near atmospheric pressure[29]. This firstly provides a real-time, rapid analysis of gas mixture streams[29]. The dynamic range, which indicates the sensitivity of detection, peaks at ~ 5 ppb[29], which allows for the detection of extremely low concentrations of analytes. There is also a large mass range, between 0-200 atomic mass units (amu)[29]. This method provides an advantage compared to FT-IR, where it can be difficult to identify samples within a mixture and is subject to spectral interference[10].

These three features combined provide a broad measurement capacity for CCUS solvents. Figure 1 illustrates the Hiden analytical mass spectrometer and Parr high pressure compact reactor[30] to contain the solvent.

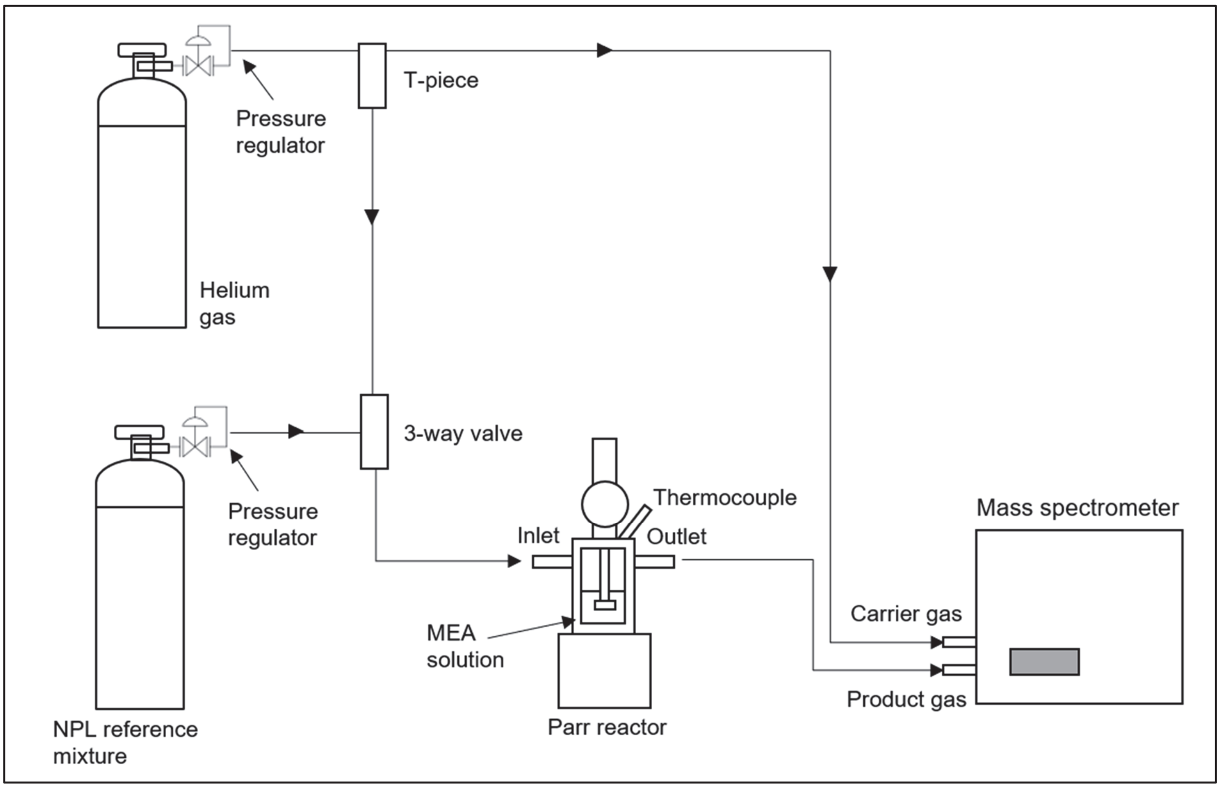

Figure 1. Schematic illustrating the NPL-MTF.

Thus, this report aims to describe the traceable method development for performance testing of carbon capture solvents, by using MEA as a benchmark solvent, under post-combustion capture conditions. This unit will be referred to as the NPL materials testing facility (MTF).

2 EXPERIMENTAL

2.1 PRIMARY REFERENCE MATERIALS AND CALIBRATION GAS

The NPL's PRM containing 15 cmol/mol CO_2 in nitrogen and 100% pure CO_2 (supplied from BOC, UK) was used for the carbonation experiments with MEA. The 15 cmol/mol CO_2 in nitrogen PRM was prepared in 10L, aluminium, spectraseal, BS14 cylinders by gravimetric method in accordance with ISO 6142-1:201531[31] using high purity CO_2 (≥ 99.9995 % purity, BOC, UK). ISO 6142-1:2015 is applicable to mixtures of gaseous or totally vaporized components added gravimetrically for the preparation of reference gas mixtures in cylinders with traceable values for the amount fraction of one or more components. The components used are typically of the highest purity commercially available, and purity analysis was performed to identify and quantify any impurities present. The compounds were added to the cylinder by direct transfer via a 1/16-inch external diameter stainless steel tubing and an NPL-designed outlet diaphragm valve (Rotarex Ceodeux, Luxembourg) that includes an internal screw thread to minimise dead volume. Where direct transfer was not possible, suitable transfer loops were used to transfer fixed amounts of gas into the cylinders via the NPL's diaphragm valve. The cylinders were weighed after each component addition was complete and the amounts recalculated to arrive at the target composition of the mixtures. The mixtures were heated and rolled in the horizontal position for two hours to achieve homogeneity of the PRM. The compositions of the mixtures (amount fraction and associated uncertainty of each compound) were calculated using the software package 'GravCalc2'. The PRM was validated by using standard NPL methods before being used for the carbonation experiments.

A set of calibration gases of the composition, 5 cmol/mol, 15 cmol/mol and 100 cmol/mol CO_2 in N_2 matrix were also prepared and validated by following the procedure mentioned above.

2.2 ONLINE MONITORING OF REACTION

Hiden Analytical HPR-20 quadrupole mass spectrometer was used for online, continuous gas analysis to monitor the composition of the gas during the DAC experiments. The gaseous analyte is ionised via electron impact (EI) through thermionic emission of the filament. The ionised samples travel through a mass filter to select species for detection through a secondary electron multiplier (SEM) [13][14]. Calibration was carried out using NPL PRMs (5 cmol/mol, 15 cmol/mol and 100 cmol/mol CO_2 in N_2 matrix) and the calibrated response of the analyser for the PRMs was within a correlation coefficient of greater than 0.95. The data was recorded using the CATLAB / MASsoft software. The instrument was used to monitor concentration variation in NPL's PRM gas mixture after interaction with the sorbent during entire course of the DAC experiments.

2.3 EXPERIMENTAL SETUP USED FOR CARBONATION EXPERIMENTS

MEA was procured from (Sigma-Aldrich, Gillingham, UK, ≥98%, CAS:141-43-5) and used without further purification. Deionised water (18.2 μScm^{-1} at 20 °C, 3 nmol/mol total organic carbon) was used for all the experiments to make an aqueous solution of 5M and 3M MEA (corresponding to 30.5 and 18.3 wt. % of MEA). For the sake of this report, these mixtures will be referred to as 3M and 5M MEA solutions. No efforts were made to remove dissolved CO_2 that was already present in the DI water for all the experiments. Figure 1 below shows a schematic of the setup used for the carbonation experiments under the NMS project. A 100 mL Hastelloy high-pressure compact reactor (5500 series compact Parr reactor, USA) fitted with a stirrer and a temperature controller unit. The reactor is interfaced with an online monitoring system that records data from a mass spectrometer instrument (Figure 1). The reactor was used as a chamber to facilitate the interaction of the MEA solution with 15 cmol/mol NPL PRM and pure CO_2 gas procured from BOC, UK. The PRM cylinder was connected to reactor as shown in the schematic (Figure 1). The product gas after interaction with the MEA solution exits the reactor to enter the mass spectrometer where it gets analysed and the data get recorded on the CATLAB software provided by Hiden. The direction of the flow of gases are indicated by the arrows in Figure 1.

2.4 VALIDATION OF EXPERIMENTAL SETUP AND BASELINE TESTS

The validation experiments were carried out to determine the amount of CO_2 that was present in the absence of the experimental gas mixture (15 cmol/mol CO_2 in N_2 PRM and pure CO_2). A zero gas (helium in this case) was analysed by the MS by flowing the gas through the empty reactor, which was closed and tested for any leaks using an electronic leak detector. The mass spectrometry response was recorded for 30 minutes. The partial pressure of CO_2 obtained from this measurement ($p_{CO2\ background}$) was used to correct the amount fraction of CO_2 measured during the carbonation experiments (equation 1). Relative sensitivity factor, RS_{CO2} of 1.01 (taken from the Hiden database)[15] is the unique ionizability of CO_2 in the mass spectrometer. The amount fraction of CO_2 was determined through the partial pressure reading of CO_2 given by the mass spectrometer, with the equation[15] for quantifying the amount fraction given in equation 1. The value was multiplied by 10000 to convert the percentage concentration to μmol/mol.

$$Amount\ fraction\ of\ CO_2\ (cmol/mol) = \left(\frac{\left(\frac{p_{CO_2\ experimental} - p_{CO_2\ background}}{RS_{CO_2}}\right)}{p_{total}}\right) \times 100 \qquad (1)$$

$p_{CO2\ experimental}$ = partial pressure of CO_2 from the experiment.
$p_{CO2\ background}$ =partial pressure of CO_2 during the helium background experiment.
RS_{CO2}= relative sensitivity of CO_2.
p_{total} = partial pressure of all the gases in the analyte mixture.

The total uncertainty in the amount fraction of CO_2 (cmol/mol) was calculated by using the expression given in equation (2). The uncertainties for $p_{CO2\ experimental}$ and $p_{CO2\ background}$ were calculated to be 0.2% of the measured partial pressure of CO_2 for experimental and background experiments respectively.

$$U_{Total} = \sqrt{\left(Up_{CO_2\ experimental}\right)^2 + (U\ p_{CO_2\ background})^2 + (Up_{total})^2} \qquad (2)$$

U_{Total} = Total uncertainty of the amount fraction of CO_2.
$U_{pCO2\ experimental}$ = Uncertainty in $p_{CO2\ experimental}$, K=2 (µmol/mol)
$U_{pCO2\ background}$ =Uncertainty in $p_{CO2\ background}$, K =2 (µmol/mol)
$U_{p\ total}$ =Uncertainty in p_{total}, K=2 (µmol/mol)

Baseline tests were carried out with DI water to determine the amount of CO_2 uptake by DI in the absence of MEA under the given experimental conditions by flowing 15 cmol/mol CO_2 in N_2 PRM and pure CO_2 for 30 minutes. This amount was subtracted from the amount of CO_2 uptake from the MEA solution under similar conditions to arrive at the carbonation efficiency of the MEA solution. DI water (50 mL) was added into the reaction vessel and closed airtight by checking for leaks using an electronic leak detector. This was necessary to ensure that CO_2 gas which was analysed by the MS was not being lost. The mass spectrometer response was recorded for the duration of flow of the reaction gases for each of these validation experiments and baseline tests.

2.5 CARBONATION EXPERIMENT DESIGN

Carbonation experiments were carried out using the setup shown in the schematic (Figure 1). The concentration of MEA and the concentration of the CO_2 gas used were varied to elucidate the effect of each on the carbonation reaction.
A volume of 50 mL of 5M or 3M MEA aqueous solutions prepared in DI water was taken in the reactor and was closed to leak tight conditions. Pure Helium gas was bubbled through the MEA solution for about 8-10 min to flush out any remnant gases within the setup. Helium gas was then switched with either of the two gases, pure CO_2 or NPL PRM containing 15 cmol/mol CO_2 in N_2 at 40 mL/min at room temperature (~ 20 ℃) for 30 minutes. The reaction mixture was stirred with a magnetic stirrer (set at '2' on the controller) for homogenisation. Each experiment was repeated once to check for reproducibility with the experimental conditions summarised in Table 2. The CO_2 and PRM gas, after interaction with the MEA solution was analysed, and data was recorded using the CATLAB /MASsoft software as described earlier. To ensure changes in experimental readings are due to the MEA solution, a baseline test with water, and a test with the empty reactor was undertaken and accounted for under each experimental condition.

2.6 CALCULATION OF CARBONATION EFFICIENCY/ABSORPTION CAPACITY BY MEA SOLUTION

The carbonation efficiency/absorption capacity expressed in moles of CO_2 per mole of MEA for the reaction of the 3Mand 5M MEA solution with NPL PRM and pure CO_2 was calculated using equation (3)[32, 33] and the total uncertainty involved was calculated using equation (4).

$$A_c = \frac{PM}{RTm} \int_{t_i}^{t_f} c_o Q_o - c_i Q_i \, dt \tag{3}$$

Where;
A_c= absorption capacity of MEA,
P = pressure of system (P = 4 bar)
M = molecular weight of CO_2 (M = 44.009 g mol^{-1})
R = molar gas constant
m = mass of MEA within reactor
T = temperature of reaction
t_f = time at the end of the experiment
t_i = initial time
c_o = outlet gas concentration (taken to be the concentration of gas analysed after the reaction with MEA)
Q_o = outlet gas volumetric flow rate (taken to be the flow rate of gas after the reaction with MEA)
c_i = inlet gas concentration (taken to be the concentration of gas from the water baseline)
Q_i = inlet gas volumetric flow rate (taken to be the flow rate of gas from the water baseline)

The total uncertainty in is given by

$$U_{total} = A_c \sqrt{\left(\frac{U_P}{P}\right)^2 + \left(\frac{U_m}{m}\right)^2 + \left(\frac{U_T}{T}\right)^2 + \left(\frac{U_{co}}{c_o}\right)^2 + \left(\frac{U_{c_i}}{c_i}\right)^2 + \left(\frac{U_{Qo}}{Q_o}\right)^2 + \left(\frac{U_{Q_i}}{Q_i}\right)^2} \tag{4}$$

Where;
U_P = Uncertainty in pressure of system (P = 4 bar)
U_m = Uncertainty in mass of MEA within reactor
U_T = Uncertainty in temperature of reaction
U_{c_o} = Uncertainty in outlet gas concentration (taken to be the concentration of gas analysed after the reaction with MEA)
U_{Q_o} = Uncertainty in outlet gas volumetric flow rate (taken to be the flow rate of gas after the reaction with MEA)
U_{c_i} = Uncertainty in inlet gas concentration (taken to be the concentration of gas from the water baseline)
U_{Q_i}= Uncertainty in inlet gas volumetric flow rate (taken to be the flow rate of gas from the water baseline)

Table 2. Experimental conditions for carbonation reactions of 3M and 5M MEA solution with pure CO_2 and NPL PRM containing 15 cmol/mol of CO_2 in N_2 reference gas mixture.

Amount of MEA	Gas composition (%)	Temperature (℃)	Reactant gas, flow rate (ml/min)	Duration (minutes)
50 mL, 3M	NPL PRM	20	40	30
50 mL, 5M	NPL PRM	20	40	30
50 mL, 5M	NPL PRM	20	40	30
50 mL, 5M	Pure CO_2	20	40	30

50 mL, 3M	NPL PRM	20	40	30
50 mL, 3M	Pure CO_2	20	40	30

3 RESULTS AND DISCUSSION

3.1 EVOLUTION OF CARBON DIOXIDE IN PRODUCT GAS AS A FUNCTION OF EXPOSURE TIME TO MEA SOLUTION

Carbonation experiments were carried out as described under the experimental section 3. The solution with 5M MEA showed a greater uptake of CO_2 in comparison to the empty reactor or DI water.

Figures 2 and 3 illustrate the CO_2 amount fraction (cmol/mol) in the product gas after interaction with 3M and 5M solutions with NPL PRM containing 15 cmol/mol of CO_2 in N_2 respectively. The curves for the experiments and their repeats are laid alongside the product gas formed analysed with an empty reactor and with 50 mL DI water for comparison. Larger amounts of CO_2 sorption by the MEA solutions (indicated by the decrease in CO_2 amount fraction) in comparison to the empty reactor or the DI water was observed. DI water also showed greater CO_2 sorption compared to the empty reactor. The CO_2 concentrations appear to increase slightly after 10 minutes of interaction with the empty reactor and DI water indicating that there is a relative decrease in the CO_2 sorption/adsorption over time. However, in the case of the MEA solutions, there is a stabilisation period for carbonation up to about 14 minutes and then the uptake is constant for the rest of the reaction time as seen in Figure 2 and 3. Continuing the experiments for a longer time would help one to find the saturation point/a steady state equilibrium achieved for the carbonation reaction known as breakthrough point. At this stage, we are unable to determine the effect of MEA concentration on the extent of carbonation simply because we haven't been able to reach the saturation point under a reaction time of 30 minutes.

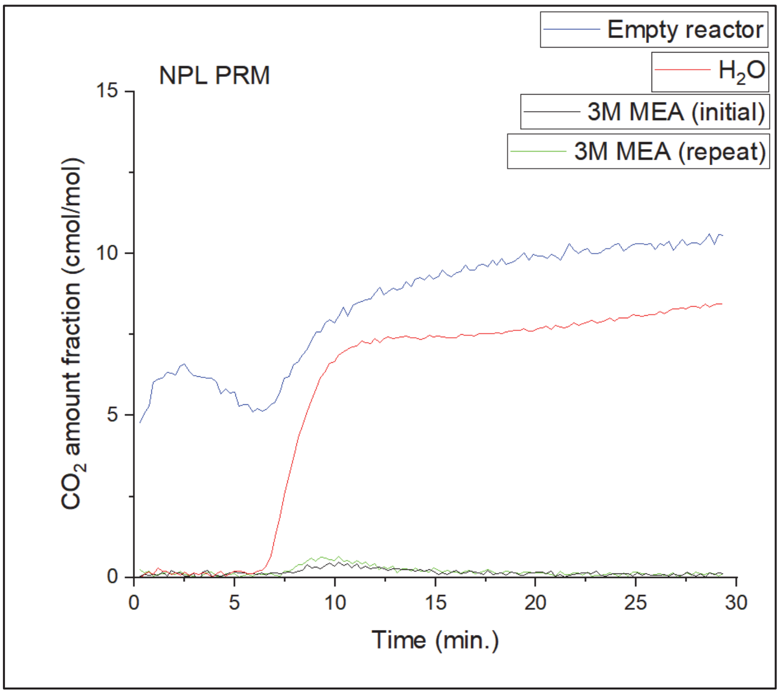

Figure 2. CO_2 amount fraction against time, 3M MEA with NPL PRM (containing 15 cmol/mol of CO_2 in N_2.

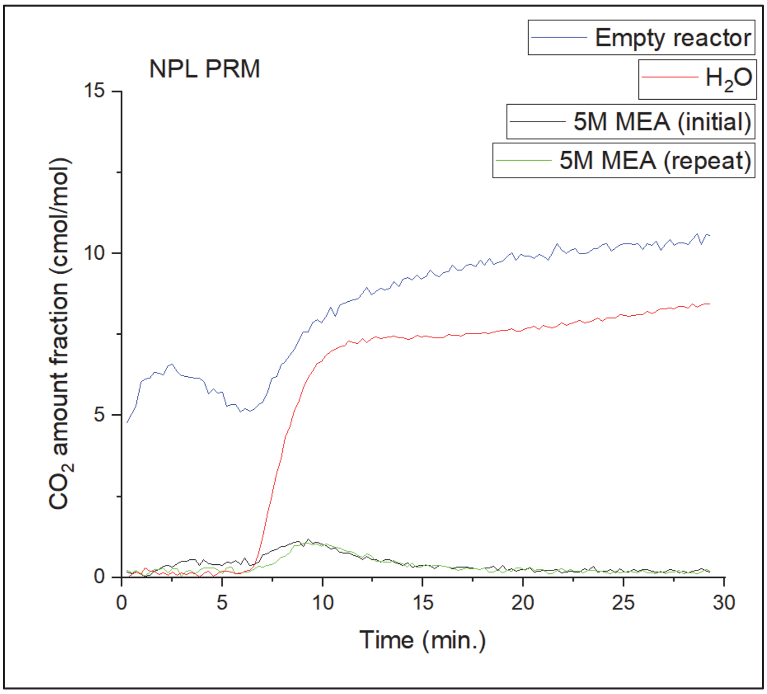

Figure 3. CO_2 amount fraction against time, 5M MEA with NPL PRM (containing 15 cmol/mol of CO_2 in N_2.

The carbonation experiments of 3M and 5M MEA solutions with pure CO_2 are shown in Figure 4 and 5 respectively. The baselines for all the experiments are not close to 'zero' cmol/mol of CO_2 indicating that more time should have been allowed to flush out all the remnant gases in the system with He prior to switching to the pure CO_2. It was also noticed that the time when the pure CO_2 gas was switched for He was not coinciding for the experiments with MEA solution, empty reactor and the blank reactions with water. The carbonation reaction being instantaneous saturates the MEA solution even before the MS response stabilises and plateaus at about 80 cmol/mol. Therefore the carbonation experiments with pure CO_2 look different from the carbonation experiments carried out using the NPL PRM (15 cmol/mol of CO_2 in N_2). One more evidence for the rapid carbonation reaction happening with pure CO_2 was the sudden increase in the reaction mixture temperatures by 4 to 7 °C in contrast to the reactions of MEA with NPL PRM that gave rise to a maximum of 0.4 °C increase in temperature for the various trials. Since the experiments with pure CO_2 are too quick to be monitored using the current online monitoring system and the post-combustion carbon capture involves about 14 cmol/mol CO_2 and therefore, future experiments/method development will involve testing of CO_2 sorbents/ sorbent using PRMs containing about 14 -15 cmol/mol CO_2 in N_2/air.

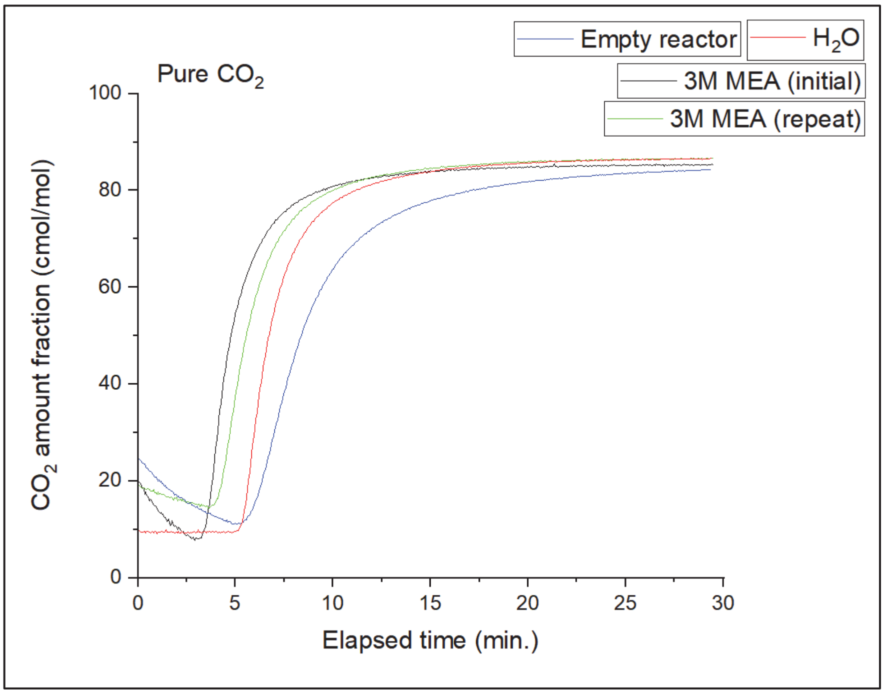

Figure 4. CO_2 amount fraction against time, 3M MEA with pure CO_2.

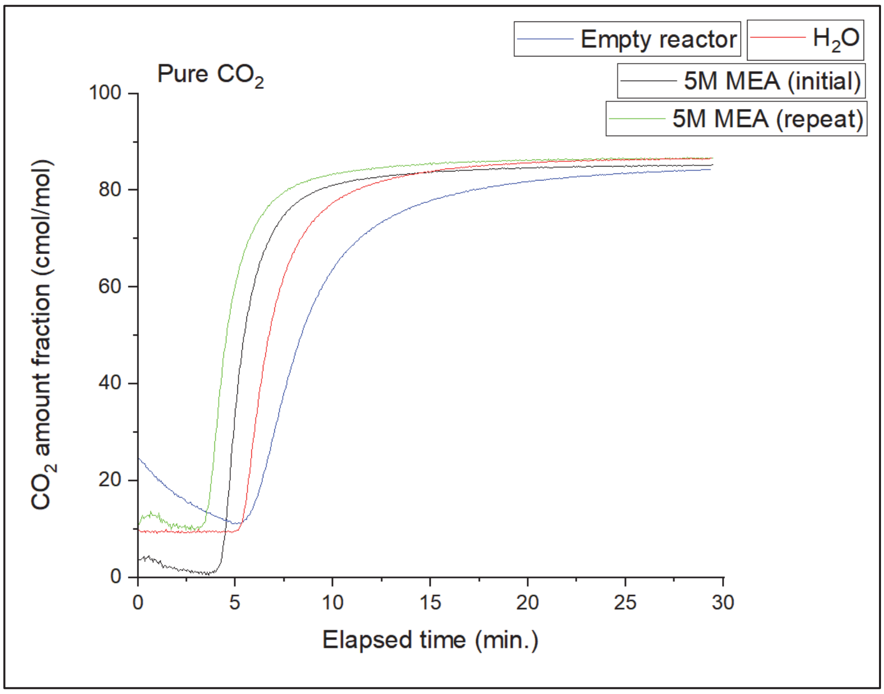

Figure 5. CO_2 amount fraction against time, 5M MEA with pure CO_2.

The absorption capacity in terms of moles of CO_2 absorbed per mole of MEA for the 3M and 5M MEA solution was calculated using equation (3). The absorption capacity for 3M and 5M MEA aqueous solutions on interaction with NPL PRM and pure CO_2 are shown in Figures 6 and 7, respectively. The experiments with NPL PRM containing 15 cmol/mol of CO_2 in N_2 showed absorption capacities varying in the range of 0.40 to 0.42 moles of CO_2 for one mole of MEA. However, experiments with pure CO_2 showed absorption capacities varying in the range of 0.34 to 0.60 moles of CO_2 for one mole of MEA. The experiments and the repeats showed greater repeatability for the experiments carried out with NPL PRM when compared with the experiments carried out with pure CO_2 under similar conditions.

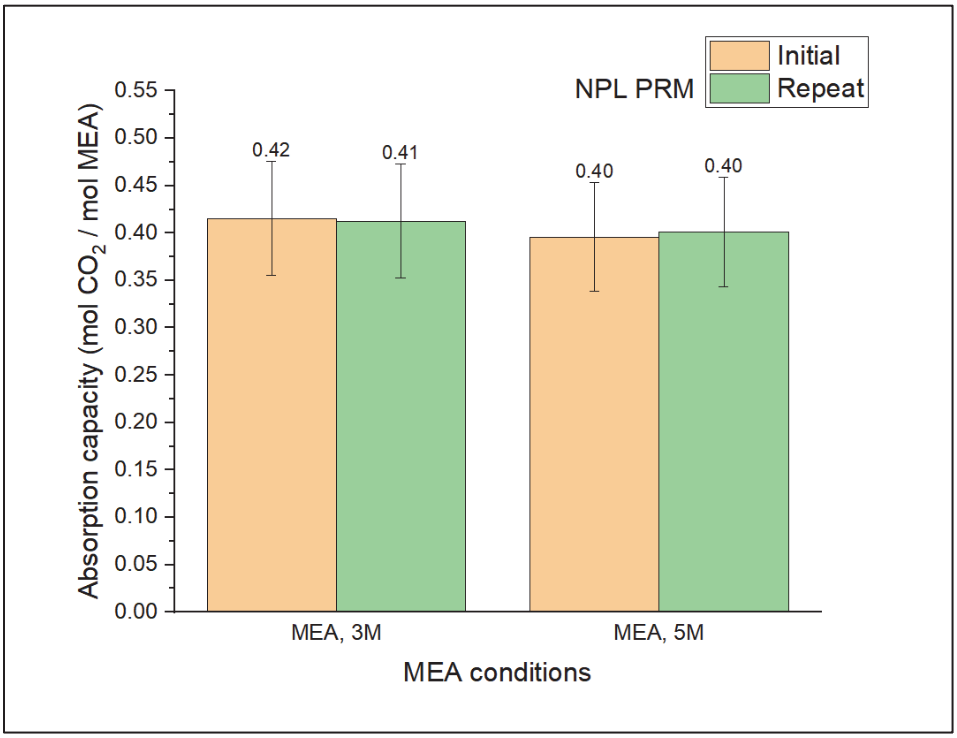

Figure 6. CO_2 absorption capacity for 3M and 5M MEA solution on interaction with NPL PRM.

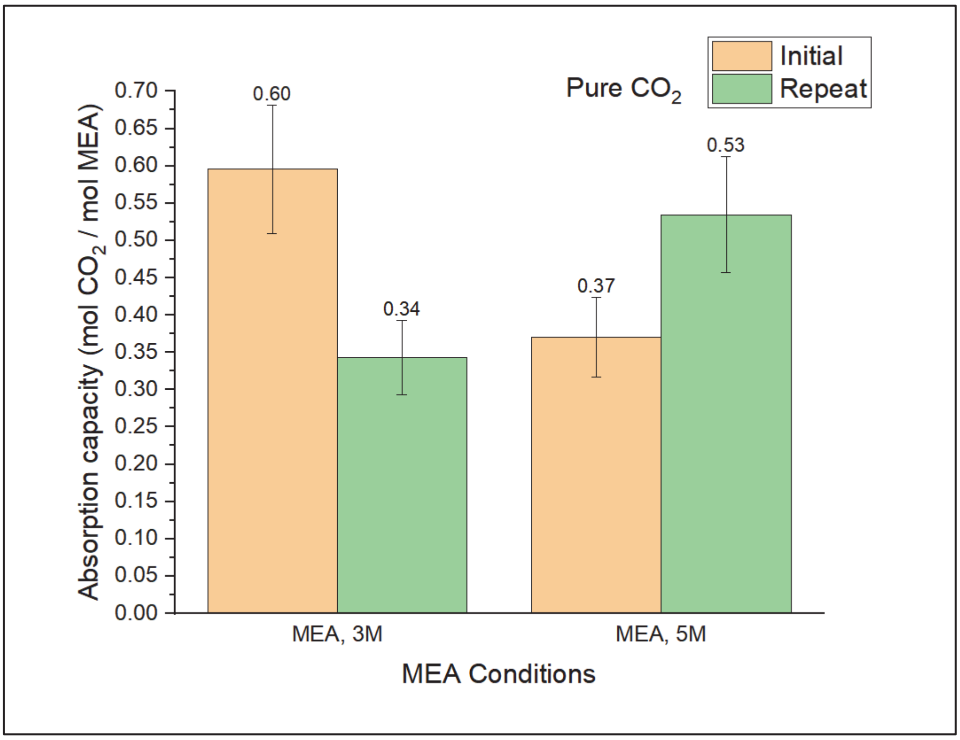

Figure 7. CO_2 absorption capacity for 3M and 5M MEA solution on interaction with pure CO_2.

The uncertainties of the moles of CO_2 absorbed per mole of MEA were calculated using an uncertainty budget method[35], using equation (4) as the measurement model. The variables' standard deviation was calculated, and converted to a standard error, which was used to a relative uncertainty value (*i.e.*, an uncertainty as a percentage). This was standardised to give a standard relative uncertainty. Finally, the standard relative uncertainties were summed in quadrature to give a combined relative standard uncertainty and multiplied by the correct coverage factor to give a 95 % confidence interval. The central limit theorem[36] was assumed throughout. The uncertainties could be improved in future work through repetition or a more accurate pressure reading, as the pressure produces the largest relative uncertainty value. A simplified uncertainty budget is given in Table 4.

Table 4. Uncertainty budget for the absorption capacity of MEA using the reactor.

Source of uncertainty	Relative uncertainty value (%)	Probability distribution	Divisor	Relative standard uncertainty (%)	Contribution to combined standard uncertainty (%)
Pressure, P	12.50	Rectangular	$\sqrt{3}$	7.22	7.22
Temperature, T	8.37	Rectangular	$\sqrt{3}$	0.12	0.12
Mass of solvent within bubbler, m	0.33 (5M), 0.55 (3M)	Rectangular	$\sqrt{3}$	0.19	0.19
Concentration of inlet stream, c_i	0.50	Rectangular	$\sqrt{3}$	0.29	0.29
Volumetric flow rate of inlet stream, Q_i	0.50	Triangular	$\sqrt{6}$	0.20	0.20
Concentration of outlet stream, c_o	0.50	Rectangular	$\sqrt{3}$	0.29	0.29
Volumetric flow rate of outlet stream, Q_o	0.50	Triangular	$\sqrt{6}$	0.20	0.20

Combined standard uncertainty = 8.70 %
Expanded uncertainty ($k = 2$) = 17.41 %

3.2 BENCHMARKING WITH OTHER LITERATURE REPORTS

The values for absorption capacities expressed in moles of CO_2 per mole of MEA for the carbonation reaction are in good agreement with the values reported in literature. Rinprasertmeechai et al.[33] used 50 mL of 4.91 M (30 wt. %) aqueous MEA at 298 K and atmospheric pressure to give an absorption capacity of 0.45 mol CO_2/mol MEA, for a 15 % CO_2, 5 % O_2, and 80 % N_2 mixture at a flow rate of 50 ml/min. Kim et al.[34] used 4.91 M at 313 K (30 wt. %) aqueous MEA at atmospheric pressure and reported a CO_2 absorption capacity of 0.57 mol CO_2/mol MEA using 30 % CO_2 in N_2 at a flow rate of 1 L/min.

3.3 SCOPE FOR FUTURE WORK

An agreement of the results of the preliminary experiments carried out using the NPL's MTF with the literature reports validates the set-up for testing carbon capture solvents. A few immediate tests will involve;

- Applying these methods to access capture capacity of various industrially used amine solvents. As a concoction of various amine solvents are currently used industry, either these samples can be taken from industry or produced commercially and made at NPL starting from commercially available solvents to match the composition used in industry.

- Effect of two crucial impurities in the post combustion flue gas present in industry will be tested under the next year NMS CCUS Net-Zero project.

- Cycling experiments involving repeated carbonation-decarbonation cycles of the MEA will also be investigated to determine the stability of the solvent and activity decay with time[21].

- Investigate the presence of degradation products as impurities from the reaction of CO_2 with MEA. This could be analysed by changing the multiple ion detection feature on the software to identify the *m/z* of common degradation products. NPL PRMs containing these degeneration products will give rise to an accurate and traceable estimation of their quantities in the emissions of various CCUS technologies.

- Accelerated aging of the solvent can be done using the current setup to study/monitor degeneration products and solvent stability[21].

- Variation of other experimental parameters leading to optimisation and solvent efficacy in carbonation reaction can be explored.

The work done under the NMS CCUS Net-Zero Uplift project will help to gain better understanding about carbon capture technologies. Standardised method for assessing the carbon capture efficiency of various sorbents/solvents using NPL PRMs along with an uncertainty budget is being developed. Moving forward, the standardised methods developed will support UK's CCUS industries and SMEs to develop safe, economic and sustainable CCUS technologies. The research finding will feedback into regulatory bodies for framing, implementing and regulating policies related to CCUS technologies. Comparison of different CCUS technologies using standardised methods developed at NPL using NPL PRMs will help the UK's funding agencies to make informed decisions before funding a particular CCUS technology.

4 SUMMARY

This report outlines the traceableCO_2 materials testing facility (MTF) , by using MEA as a benchmark solvent, under post-combustion capture conditions. The results obtained on the NPL "MTF" to determine CO_2 capture capacity of MEA aqueous solutions is in good agreement for the values reported in literature under similar conditions. The advantage of the NPL "MTF" is the reliability of the test and the traceability of the measurement to NPL PRMs. The uncertainty determination was good achieving an expanded uncertainty of 14.48% (k=2) for CO_2 capture capacity per mole of MEA.

Through these preliminary experiments, NPL demonstrated and validated the ability of the "MTF" to support industry in evaluating carbonation reaction of relevant carbon capture solvents under different experimental conditions. The selection of the most relevant carbon capture solvent is a key element to progress and enable the deployment of reliable large scale carbon capture system industrially.

Future works aim at evaluating a large panel of industrially relevant solvents and conditions to expand the current knowledge and provide metrological guideline in the realisation of the tests. Experiments involving effect of impurities, solvent regeneration, cycling, accelerated aging to identify, quantify and monitor any degeneration products will be carried out in the next phase. The work will have great impact in the safe, effective and sustainable deployment of CCUS technologies besides assisting the UK government to reach its Net-Zero objectives by 2050.

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