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Experimental approach to mimic and study degradation of solvents used for post-combustion CO_2 capture

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Abstract

A degradation experimental protocol with 30%-wt MEA solvent has been applied successfully on a lab-scale experiment set up to simulate the operating conditions seen by the solvent during cycles of absorption and stripping of the CO_2 capture process. Degradation campaign lasted about 750 hours (750 cycles) in the presence of a synthetic flue gas containing 82% of N_2, 15% of CO_2, 3% of O_2. An important number of degradation products (more than 30) was detected and most of the species were identified in agreement with literature.

Keywords: CO_2 capture, MEA degradation, absorber and stripper conditions, lab-scale experiment.

1. Introduction

One key criterion of CO_2 capture solvents is their resistance to ageing – a set of thermal and chemical mechanisms - leading to a degradation of the process optimal operation and possible emissions. Indeed during the CO_2 absorption-

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stripping process, irreversible reactions may occur resulting in the formation and the accumulation of degradation products in the solvent and consequently the reduction of the process optimal operation and possible emissions [1], [2], [3].

In order to answer this issue, EDF R&D decided to set up a lab to reproduce and study the degradation of solvents used for CO_2 capture, named "LEMEDES-CO_2". In particular, LEMEDES-CO2 lab-scale apparatus has been designed to reproduce the dynamic cycling of the solvent between the absorber and the stripper columns. The technical features of this original lab-scale apparatus were based on the chemical absorption principle with short cycles of absorption and stripping, fast heating up and cooling down of the solvent and an important gas flow rate (1800 NL/h). The experimental approach is essential and serves several purposes: identification of degradation products in the process effluents, understanding of their generation and development of knowledge about solvent characterization.

Within the framework of a French-funded R&D project (named DALMATIEN for Degradation of Amines in Liquid Matrix and Analysis: Toxicity or Innocuousness for ENvironment?) an experimental protocol of degradation was developed for 30 wt % MEA. The experimental conditions were chosen according to representative industrial conditions of post-combustion amine-based capture systems.

This paper focuses on description of this experimental protocol and the obtained degradation products in order to confirm the test-bed capacity to reproduce the ageing phenomenon observed at industrial scale with MEA

2. Material and methods

2.1. Chemicals

Ethanolamine (MEA) (98%), Hydranal-Composite 5K and methanol dry were purchased from Sigma-Aldrich (Saint Quentin Fallavier, France).

2.2. Lab-scale experiment description

The LEMEDES-CO_2 lab-scale experiment has been based on the chemical absorption principle. The test bed was composed of: a semi-batch glass reactor (open on the gas side) where the solvent was brought into contact with a synthetic flue gas, an heat exchanger supplied with mineral oil enabling a fast heating up and cooling down of the solvent (for temperature control), piping to circulate the solvent between the reactor and the heat exchanger, and outlet piping to exhaust the outlet gas (including pressure control) and a gas blender to control flow rates and composition of the synthetic flue gas. All piping was made of hastelloy in order to uncouple oxidation and corrosion phenomenon. This facility was able to handle a pressure up to 6 bara. The control system followed many parameters such as pH, gas composition, conductivity and, operated continuously and automatically (24h/24 and 7d/7). Gases analyzers were connected to continuously follow outlet gases concentration. Samples were taken from the liquid and gas phase and analyzed at regular intervals.
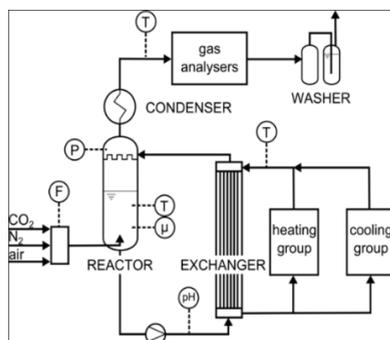

Fig. 1. Scheme of the LEMEDES-CO_2 lab-scale experiment

The experimental conditions were chosen to be representative of industrial conditions of post-combustion amine-based capture systems. An experimental procedure has been developed for 30 wt % MEA in water. The synthetic flue gas composition was CO_2 15% N_2 82% and air 3%. Gas flow rate was 1800 NL/h and liquid flow rate was 5 L/min. Absorber temperature was set at 50°C at atmospheric pressure and stripper temperature was set at 120°C at 4 bara (stripping was carried out by N_2 injection). The total volume of solvent was 1.5 L. The duration of a cycle of absorption and desorption was less than one hour. The ageing campaigns lasted at least one month (750 cycles, about 750 hours).

2.3. Analysis

- Water content measurement

The water content of the amine blend was measured using a V20 Karl Fisher (Mettler). The reagent used for the titration were Hydranal-Composite 5K (Sigma Aldrich) and Methanol dry (Sigma Aldrich).

- Gas sampling and solid phase extraction

Solid phase extraction of gaseous compounds was performed during 25 min of the absorption phase with two types of adsorbent Tenax TA TDU tubes (Chromoptic,Villejust, France) and activated charcoal tubes CarbopackTM B/CarbopackTM (Chromoptic,Villejust, France). Tenax TA is based on 2,6-diphenylene oxide polymer. Gas samplings have been conducted after the condenser with an ambient air sampler from Supelco. The gas flow was 0.2 L/min. Sampling were scheduled at the end of the campaign. Three consecutive Tenax TA tubes were used to limit breakthrough phenomenon. Tenax TA tubes and activated charcoal tubes were then thermally desorbed as described in the GC-MS part. Charcoal tubes were used to confirm or infirm punctually the presence of some volatiles compounds observed with Tenax tubes. Quantification method is described in a previous work [4].

- GC-MS

For the liquid samples, analyses were performed with two GC-MS:

An Agilent 7890A gas chromatograph coupled with a Jeol JMS-Q1000GC mkII Ultraquad mass spectrometer (Jeol, Croissy, France) was used. A non polar fused silica capillary column CP-SIL8 CB-MS (30 m x 0.25 mm x 1 µm) was used. The chromatographic method was: initial temperature was 40°C held for 2 min then raised to 130°C at 7°C/min, increased to 280°C at 13° C/min and held for 10 min. Helium was used as carrier gas in constant flow mode at 1 mL/min. The transfer line temperature to the MS detector was set at 280°C. For liquid injection procedures, real samples were diluted 10 times in methanol before injecting 1 µL in split mode (1:5) at 250° C.

Analyses were performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C inert XL MSD mass spectrometer (Agilent Technologies, Massy, France) too. The device was equipped with a MPS (MultiPurpose Sampler) auto sampler from Gerstel (RIC, Saint-Priest, France) that enabled fully automated HS-SPME analyses. Two columns (Chromoptic, Villejust, France) were used to separate the compounds, a non-polar fused silica capillary column CP-SIL8 CB-MS (30 m x 0.25 mm, 1 µm) and a polar fused silica capillary column DB-WAX (30 m x 0.25 mm, 0.5 µm). For the non-polar column, initial temperature was 40°C held for 2 min, then raised to 130°C at 7°C/min, increased to 280°C at 13°C/min and held for 10 min. For the polar column, oven temperature program started at 40°C, held for 2 min, then raised to 130°C at 7°C/min, then increased to 200°C at 10°C/min and held for 7 min. In both cases, helium was used as carrier gas in constant flow mode at 1 mL/min. The transfer line temperature to the MS detector was set at 280°C. For liquid injection procedures, real samples were diluted 10 times in methanol before injecting 1µL in split mode (1:5) at 280°C. Detection was performed with a mass spectrometer using electronic ionization (EI) source (70 eV) heated to 250°C. The scan range was 25 to 250 amu.

For both GC-MS,NIST spectra data base was used for the pics identification.

For thermodesorption of tubes (after gas sampling), gas flow rate of helium was 40 mL/min in splitless mode. Initial temperature of desorption was 35°C held for 2 min then raised to 300°C at 120°C/min and held for 6 min. Desorbed molecules were cryofocused in the injector at−40°C with liquid CO_2. Then temperature increased from 40°C to 300°

C at 12 ◦C/s and the molecules were injected in the column in splitless mode. The same GC/MS method as for liquid samples was used.

Detection was performed with a mass spectrometer using electronic ionization (EI) source. The EI source (70 eV) was heated to 250◦C, the scan range was 25–250 amu.

- LC-MS/MS

Analysis were performed on a LC Agilent 1100 coupled with a MS Waters micromass ZQ 4000 with ESI source. It was used in positive mode with a source temperature of 120°C. The chromatographic separation was realized with a Thermo Hypercarb column (150 mm x 3 mm, 5 µm-particles). The mobile phase was composed of (A) water + ammonia to reach a pH of 10.8 and (B) Methanol + 0.1% formic acid at a flow rate of 350 µL/min. 5 µL of sample previously diluted by 100 in mobile phase A were injected. The solvent gradient started at 100% of A for 10 min before reaching a ratio of 80:20 (A:B v:v) in 8 min. This ratio was maintained for 12 min.

- HeadSpace-SPME (HS-SPME)

The fully automated HS-SPME procedure is described in a previous work [4]. This method was initially developed for identification and quantification of pyrazines [6]. It is adapted here to the identification of other degradation products present in liquid phase.

3. Results and discussion

3.1. Lab-scale experiment monitoring

Pressure and temperature in the reactor were monitored continuously as CO_2 inlet and outlet. Results showed a good reproducibility of absorption/stripping cycles during the whole campaign. Analyze of the concentration of water also enabled an estimation of water loss compensated by regular water addition in order to maintain 70% wt of water (figure 2). Furthermore an estimation of CO_2 loading (mol CO_2/mol MEA) was calculated with volumetric method (acid titration). CO_2 loading in the solvent after absorption and stripping phases were quite stable at roughly 0.42 and 0.26 mol/mol respectively for rich and lean solvent and in agreement with literature [7].
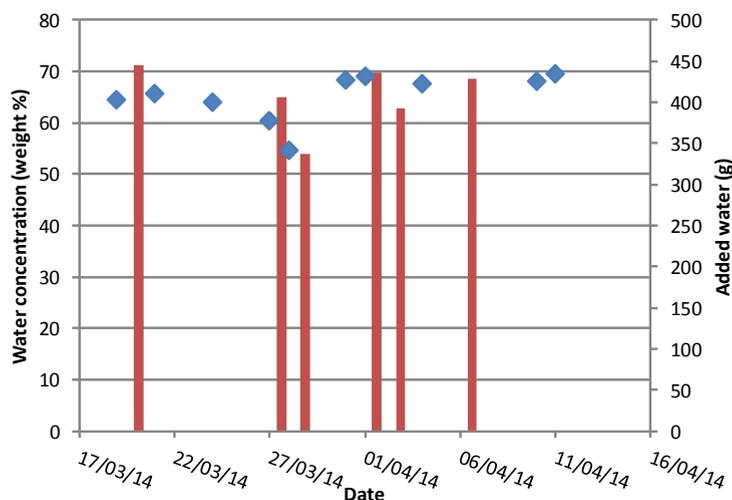

Fig. 1. Evolution of water concentration (in blue) and added water quantity (in red).

3.2. Degradation products in the solvent

More than 30 degradation compounds of the MEA have been detected with all analysis methods and most of the species are identified, in agreement with literature (see table 1) [8][9][10]. Those results showed this bench scale set up capacity to mimic observed degradation phenomenon on industrial pilot plant, thus validating the capacity of the lab-scale experiment to simulate the alternating operating conditions seen by the solvent during cycles of absorption and stripping. Furthermore, within the framework of the French-funded R&D project, our results have been successfully compared with the degradation products observed from a capture pilot plant of a partner [4].

Table 1. Degradation products in the solvent.

		Analysis methods		
		GC-MS		LC-MS/MS
Sample treatment →		Ø	HS-SPME	Ø
Products	Mw g/mol			
Ethyleneglycol (EG)	62	X		
Oxazoline	71		X	
Oxazolidine	73		X	X
Glycine	75			X
Pyrazine	80		X	X
2-Oxazolidinone (OZD)	87	X	X	
N-(2-hydroxyethyl)formamide (HEF)	89	X	X	
N-(2-hydroxyethyl)acetamide (HEA)	103	X		
Diethanolamine (DEA)	105	X		
N-(2-hydroxyethyl)pyrrole (HEpyr)	111	X	X	
N-(2-hydroxyethyl)imidazole (HEI)	112		X	
N-nitrosomorpholine	116			X
N-(2-hydroxyethyl)glycine (HEGly)	119	X		X
N-(2-hydroxyethyl)imidazolidin-2-one (HEIA)	130	X		
1-(2-hydroxyethyl)piperazin-2-one (1HEPO)	144	X		
4-(2-hydroxyethyl)piperazin-2-one (4HEPO)	144	X		
Bicine	163	X		
N,N'-(Bishydroxyethyl)oxalamide (BHEOX)	176	X		

Furthermore, seven main degradation products were quantified by GC/MS (EG, HEF, HEA, OZD, 1HEP, HEI, 4HEPO). Their concentration were globally in agreement with literature [4].

3.3. Degradation products in the gas effluent

The degradation products in gas effluents were analyzed after sampling on solid phase adsorbents as Tenax and charcoal. Gas effluent samplings were conducted after the condenser. All the species have been identified and among

them, few have just been recently identified in the frame of the R&D project [5] [6]. Table 2 presents the list of these identified degradation compounds.

Table 2. Degradation products in gas effluents.

Products	Mw (g/mol)	Tenax	Activated charcoal
Acetamide	59	X	X
Ethyleneglycol (EG)	62	X	
N,N-dimethylformamide	73		X
Oxazolidine	73	X	X
Propionic acid	74	X	
2-methylpyrazine (2MP)	94	X	X
Diethyleneglycol (DEG)	106	X	
2,6-dimethypyrazine	108		X
N-(2-hydroxyethyl)pyrrole (HEPyr)	111	X	X

4. Conclusion

A degradation experimental protocol with 30%-wt MEA solvent has been applied successfully on a lab-scale experiment "LEMEDES-CO2". A campaign of 750 hours of degradation was performed. An important number of degradation products has been detected in the liquid and gas phases and most of the species are identified thanks to a panel of analytical methods developed in the frame of the R&D project. Those results are in agreement with literature validating the capacity of the lab-scale experiment to simulate the alternating operating conditions during CO_2 capture processes and the solvent ageing phenomenon.

Acknowledgments

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