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DEGRADATION OF AMINE SOLVENTS USED FOR CO2 REMOVAL FROM FLUE GAS WITH HIGH CO_2 CONCENTRATION

Andrzej WILK [b]*, Tomasz SPIETZ [a], Lucyna WIĘCŁAW-SOLNY [b],
Aleksander KRÓTKI [a], Justyna TARNOWSKA [a]

[a] MSc; Institute for Chemical Processing of Coal, ul. Zamkowa 1, 41-803 Zabrze
[b] PhD; Institute for Chemical Processing of Coal, ul. Zamkowa 1, 41-803 Zabrze
*E-mail address: *awilk@ichpw.pl*

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Abstract

In the ethanolamine (MEA) solution, during the absorption and desorption of CO_2 undesired compounds are produced as a result of degradation of an amine. Degradation not only reduces the absorption capacity of the solution but also leads to many operational problems. Furthermore, measuring of the degradation products is of great importance in terms of environmental issues. For the determination of MEA degradation products, mainly chromatographic techniques are used, sometimes coupled with other instrumental methods, e.g. GC-MS. As a part of this work, research was conducted to identify MEA thermal and oxidative degradation products and to develop a method for quantitative analysis of the main thermal degradation products such as OZD, HEIA and HEEDA and oxidative degradation products: HEA and HEI. Samples drawn from a test bench for CO_2 capture from synthetic flue gas with an increased content of carbon dioxide were tested. As a research result, a method for the quantitative determination of the main degradation products was developed, the concentrations of degradation products and the rate of their formation were determined, which allows to qualify the solution shelf life.

Keywords: **Carbon dioxide; CCS; Degradation; GC-MS; Monoethanolamine.**

1. INTRODUCTION

The concentration of carbon dioxide in the atmosphere has fluctuated around 280 ppm over the last 10,000 years [1]. However, since the second half of the 19th century, a significant increase in the concentration of carbon dioxide in the atmosphere has been observed. Currently, the average global concentration of carbon dioxide in the atmosphere is approximately 410 ppm [2]. Analysis carried out by the Intergovernmental Panel on Climate Change suggest, inter alia, that human activity significantly contributes to the increase of CO_2 concentration in the atmosphere, which may affect climate change [3–5]. In order to counteract this, it is necessary to implement low-emission technologies with high efficiency. The "clean coal technologies" should enable the combustion of fossil fuels with a limited emission of greenhouse gases to the atmosphere.

There is a huge number of technologies in the industry that are suitable for the separation of CO_2 from fossil fuel combustion processes, such as: physical and chemical absorption, adsorption, membrane processes, cryogenic processes or the chemical loop [3], [6–12]. Of these, chemical absorption is the most developed and most commonly used method for removing CO_2 from large gas streams. The main technology of CO_2 capture using the chemical absorption method is amine absorption which is widely used in the industry to remove acid components from various types of gases [13]. The suitability of an amine absorbent for use in CO_2 removal from a given gas is determined by many parameters, such as the CO_2

absorption rate, absorption capacity [13], heat of absorption, corrosiveness or susceptibility to degradation [14, 15].

CO_2 capture technologies and further use of the released CO_2 is one of the important tools to ensure the achievement of the Green Deal goal of climate neutrality in the EU in 2050. It is important to get to know each of these process components to eliminate possible operational problems. The solvent degradation in the CO_2 capture process may cause various problems as well as the costs of used solvents replacing but also undesired degradation products emissions to the environment.

The most frequently used amine absorbent (solvent) in the CO_2 removal process is monoethanolamine (MEA) [16–18]. The CO_2 removal basically consists of two stages, i.e. absorption of CO_2 in the solvent and regeneration of rich solvent (i.e. loaded with CO_2) under the increased temperature and/or reduced pressure [19, 20].

Undesirable compounds are formed in the MEA solution as a result of both CO_2 absorption and desorption, as a result of amine degradation. Degradation not only reduces the absorption capacity of the solution, but also leads to many operational problems such as: foaming [21], corrosion [22, 23], increased solution viscosity or solid formation [24]. All this reduces the operating life of both individual components of the CO_2 capture plant and the absorbent itself. It is especially important in the case of the presence of oxygen and high CO_2 content in flue gases, as it is in the case of many industrial flue gases (cement production, metallurgy), where it can significantly affect the durability of the solutions used in the process of CO_2 capture.

The degradation can be of two types (Fig. 1): thermal or oxidative [25–27]. Oxidative degradation is the chemical reaction of amines with oxygen that enters the solution with the gas stream. This type of degradation takes place mainly in the absorption column vessel, on the column packing, in the pipelines leading to the cross heat exchanger and in the exchanger itself. Oxidative degradation breaks the carbon-nitrogen bond and forms a carbon-oxygen bond, resulting in numerous degradation products. Degradation products can react with each other and with free amine molecules resulting in the formation of further undesirable compounds. Typical products of MEA oxidative degradation are ammonia, aldehydes, ketones, amides and carboxylic acids [28]. Some of these products are highly volatile, and therefore may be emitted to the atmosphere, posing a risk to the environment [29, 30]. These products can also react with the construction materials of the plant, creating heat stable salts (HSS) which accumulate in the system, causing foaming, solid formation etc. [31, 32]. The high volatility of most of the oxidative degradation products results in that only some of these types of degradation products can be quantified in solution samples without high error. This applies to large-molecule degradation products such as HEA and HEI.

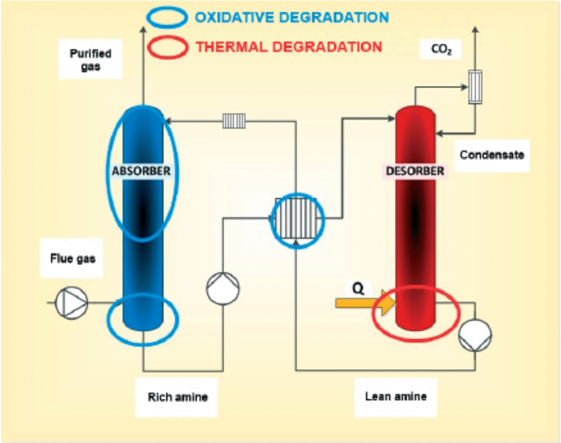


Figure 1.
Main points of degradation process occurrence in the amine scrubbing systems

Thermal degradation occurs due to elevated temperature. Most often this occurs on the regenerator packing, in the desorption column vessel and in the pipes leading from the regenerator to the cross heat exchanger. The main causes of thermal degradation include degradation of carbamates (formed during the absorption) due to the temperature of 100°C or higher [33].

Amines such as MEA, diethanolamine (DEA) and N-methyldiethanolamine (MDEA) have been used for decades in the removal of acid components from refinery gases and natural gas where, due to the lack of oxygen, the phenomenon of thermal degradation primarily occurs. Consequently, the thermal degradation products of these amines have been well characterized. The main products of thermal degradation of MEA include: oxazolidinone (OZD), N-(2-hydroxyethyl)-2-imidazolidinone (HEIA) and N-(2-hydroxyethyl)ethylenediamine (HEEDA) [28].

The largest group of analytical techniques used to determine amine degradation products are chromatographic techniques, i.e. gas chromatography (GC), liquid chromatography (HPLC), ion chromatography (IC) and chromatographic techniques coupled with other instrumental methods, e.g. gas and liquid chromatography coupled with mass spectrometry (GC-MS, HPLC-MS), gas chromatography coupled to Fourier transform infrared spectroscopy (GC-FTIR) and gas chromatography coupled to atomic emission spectroscopy (GC-AED). Among the analytical techniques mentioned, the most frequently used method is gas chromatography coupled with mass spectrometry using electron ionization (EI) and chemical ionization (CI).

Strazisar et al. [34] described the use of the GC-MS method to study the degradation products of monoethanolamine. Due to the large differences in the polarity of the compounds to be determined, two types of chromatographic columns were used to separate the degradation products. The first is a 60 meter capillary column with a diameter of 0.32 mm covered with 0.25 µm of poly(cyanopropylphenyl)(14)methyl(86)siloxane (DB-1701) film. The second is a 60-meter column with a diameter of 0.25 mm filled with 0.25 µm thick modified polyethylene glycol (NUKOL). The use of columns of different polarity allowed for the separation and determination of various types of MEA degradation products.

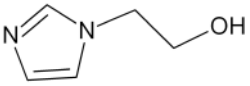
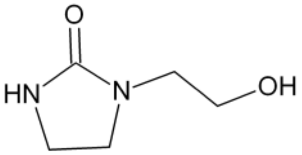
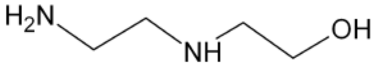
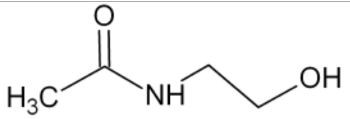
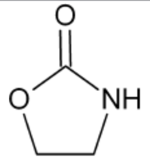
In another research paper [35], the method of gas chromatography with a mass spectrometer as a detector was used to identify the degradation products. GC-MS analysis was performed using electron ionization (EI) and chemical ionization (Cl). A CPSIL8-CB-Amines column, 30 meters long, 0.25 mm in diameter and stationary phase thickness – 1.2 µm, was used to separate the degradation products. The quantitative analysis of the identified degradation products was carried out using a gas chromatograph with a flame ionization detector (GC-FID) using two types of columns, polar – CARBOWAX-AMINES 15 m long, 0.53 mm in diameter and 1.0 µm film thickness and non-polar – CPSIL8-CB-AMINES with a length of 25 m, diameter 0.32 mm and a film thickness of 1.2 µm. The internal standard (IS) method was used as the method of quantitative analysis.

The aim of this experimental studies was to quantify the products of thermal and oxidative degradation of MEA and to develop a quantitative analysis method for their determination using chromatographic method. The quantitative analysis of the degradation products amount over time will allow to determine the useful life of the absorption solution used for CO_2 capture.

2. EXPERIMENTAL

This section describes the analytical method and used apparatus. The investigated MEA degradation products has been shown in Table 1.

Table 1.
Degradation products of MEA determined in this work

Abbr.	Name	Formula	Molar mass g/mol	CAS
HEI	1-(2-hydroxyethyl)imidazole		112	1615-14-1
HEIA	N-(2-hydroxyethyl)-2-imidazolidinone		130	3699-54-5
HEEDA	N-(2-hydroxyethyl)ethylenediamine		104	111-4-1
HEA	N-(2-hydroxyethyl)acetamide		103	142-26-7
OZD	2-oxazolidinone		87	497-25-6

2.1. CO_2 capture test bench

The samples for the analysis were drawn from the laboratory CO_2 capture test bench. This plant is characterized by continuous operation in the absorption-desorption system. The plant has capacity of 5 m^3/h of treated gas. The basic elements of the test bench are an absorption a desorption (regenerator) columns and the cross heat exchanger. The absorption and desorption columns contain glass Raschig rings packing. In the middle of the stand there is a heat exchanger that preheat the rich solvent stream flowing to the top of the regeneration column. The heat needed for the solvent regeneration is supplied to the system by an electric heater with a power supply controller. The regenerated solvent leaves the regenerator and flowing through the cooler is back to the absorber.

The inlet gas containing 30% vol. CO_2 is homogenized in the mixing chamber to which it is supplied with air from a blower. More details about the laboratory stand can be found elsewhere [36].

2.2. Chemicals and analysis

The Focus GC gas chromatograph by Thermo Scientific, equipped with a split/splitless dispenser coupled with the DSQ II mass spectrometer (GC-MS) by Thermo Scientific, operating in both SCAN and SIM modes and allowing for electron ionization (EI) was used to test the MEA thermal degradation products. A ZB-5MSi capillary column (30m x 0.25mm x 1mm) was used to separate the analytes. The NIST spectrum library was used to identify degradation products. The following reagents/standards were used for calibration: 2-Oxazolidinone, 98%, Sigma Aldrich; 1-(2-hydroxyethyl)imidazole, 97%, Sigma Aldrich; N-(2-hydroxyethyl)acetamide, 96%, Acros Organics; N-(2-hydroxyethyl)-2-imidazolidinone, 75% aqueous solution, Sigma Aldrich; N-(2-hydroxyethyl)ethylenediamine, 99%, Sigma Aldrich.

For the analysis, the rich solvent samples (loaded with CO_2) were drawn from the absorber and the lean ones (unloaded with CO_2) were collected from the regenerator, downstream of the cooler.

2.3. Analysis parameters

The conditions for the chromatographic analysis and the operating conditions of the mass spectrometer are shown in the Table 2.

Table 2.
The parameters of chromatographic analysis

Parameter	Value
Dispenser temperature	250°C
Initial oven temperature	40°C
Final oven temperature	250°C
Oven temperature increase	6°C/min
Carrier gas flow rate	1.0 ml/min
Split ratio	10
Transfer line temperature	250°C
MSD working mode	SIM/FULL SCAN
Ionization Type	Electron (EI)

The mass spectra obtained as a result of the analysis and compared with the library of spectra, (which is part of the GC-MS system software) were used to identify compounds that are products of thermal degradation of MEA. Table 3 summarizes the retention times for the individual compounds.

The internal standard method (IS) was used for quantification. Relative response factors for individual compounds were determined according to the equation:

$$RF_C = \frac{A_C \cdot M_{IS}}{M_C \cdot A_{IS}} \tag{1}$$

where: RF_c is relative response factor for each compound, A_c is peak area read for a given compound, A_{is} is peak area read for the internal standard, M_c is the content of the analyte in the reference mixture, M_{is} is the content of the internal standard in the reference mixture.

The average calculated RF_c values are presented in Table 3.

Table 3.
Average retention time and average response factor for measured compounds

Determined compound	Mean retention time for 10 repetitions, min	Mean response factor for 5 repetitions
OZD	17.25	0.505
HEDDA	14.10	0.627
HEIA	24.84	0.728
HEA	16.56	0.569
HEI	19.96	0.496

The content (M_c) of a given component in the sample (i.e. 1 ml) was calculated by converting equation (1) to M_C.

The statistical evaluation of the results included the determination of the following parameters: selectivity, calibration and linearity determination, repeatability, intermediate precision, resistance. The selectivity of the method is guaranteed by the use of a mass spectrometer as a detector, which works in the mode of monitoring selected ions (selective detector).

Calibration using an internal standard was performed based on the analysis of calibration solutions. For individual compounds, calibration curves were determined based on the following formula:

$$c_w = f\left(\frac{s_w}{s_{IS}}\right) \qquad (2)$$

where: c_w is the analyte content in the standard, s_w is peak area read for a given analyte, s_{is} is peak area read for the internal standard.

In order to determine the linearity of the method, the values of the obtained relative response factors RF_c were compared as a function of the content of a given analyte. The obtained dependence should be a linear function in which the slope is insignificantly different from zero and the value of the intercept does not differ from the mean value of the relative response factor RF_c in a statistically significant manner. The t-Student test was used to assess the linearity of the method.

The repeatability of the method was determined based on the calculated values of standard deviations for six series of samples. Each series consisted of 7 independently performed analysis. Using the propagation law, the repeatability of the method was determined. Intermediate precision was calculated as the relative standard deviation of all results for which a repeatability value was calculated (shown in Table 4).

Table 4.
Repeatability and precision for all determined compounds, expressed as the variation coefficient

Determined compound	Repeatability [%]	Intermediate precision [%]
OZD	4.99	5.76
HEDDA	3.78	4.15
HEIA	4.20	5.06
HEA	5.49	6.45
HEI	6.79	7.24

The resistance of the method was verified based on the calculated values of repeatability and intermediate precision. For this purpose, the value of the F_{max}–Hartley test statistic was calculated and compared with the critical value F_{kr}.

$$F_{max} = \frac{CV_{prc.por}^2}{CV_{powt}^2} \qquad (3)$$

where: $CV_{prc.por}$ is variation coefficient for intermediate precision, CV_{powt} is repeatability variation coefficient.

The method is resistant when the assumptions that $F_{max} < F_{kr}$ are met. Based on the calculated values of the F_{max}–Hartley test statistics for each compound, no statistically significant difference was found between the calculated repeatability and the intermediate precision. So the method is resistant.

3. RESULTS AND DISCUSSION

The results of the determined degradation products were shown in Table 5 (A3.x is rich solution A4.x stand for lean solution).

Table 5.
The results of analyzed samples

No. sample	OZD	HEEDA	HEIA	HEA	HEI
	mol/dm^3				
A3.1	0.008	0.002	0.010	0.025	0.045
A4.1	0.015	0.012	0.021	0.018	0.021
A3.2	0.012	0.008	0.018	0.033	0.068
A4.2	0.021	0.011	0.029	0.024	0.037
A3.3	0.026	0.016	0.033	0.041	0.087
A4.3	0.048	0.024	0.048	0.028	0.074
A3.4	0.035	0.021	0.040	0.087	0.099
A4.4	0.052	0.048	0.064	0.034	0.076
A3.5	0.037	0.029	0.054	0.067	0.084
A4.5	0.058	0.048	0.073	0.052	0.070

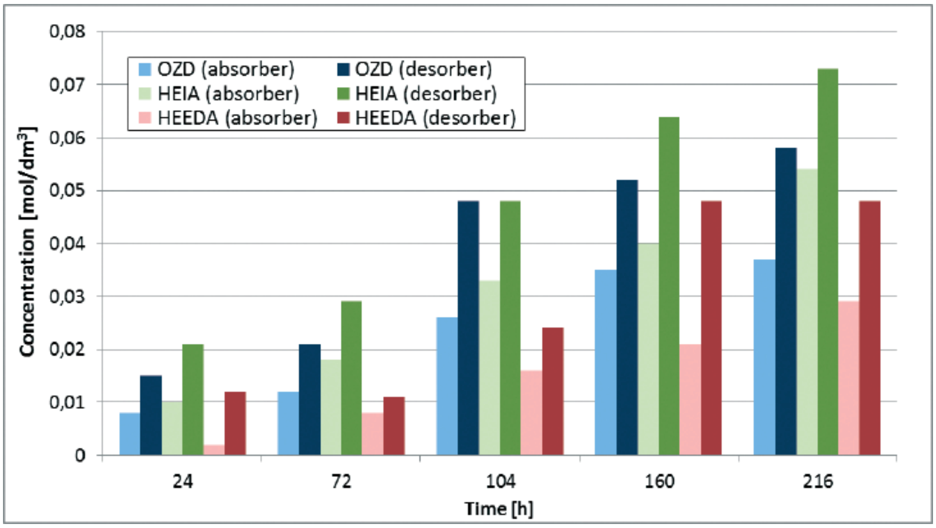


Figure 2.
Major degradation products of MEA formed in absorption and desorption columns

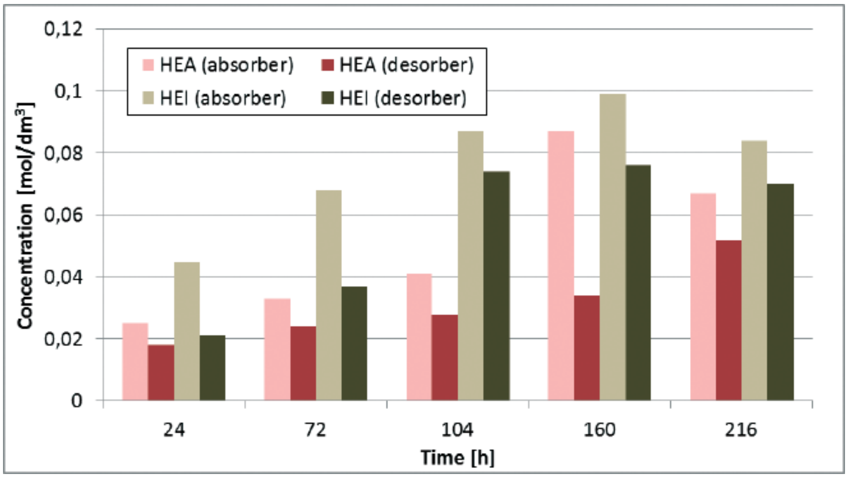


Figure 3.
Comparison of high molecular oxidative degradation products of MEA formed in absorption and desorption columns

The samples were collected periodically during the CO_2 capture process. From table 5 it can be seen that rich solvent samples contain more HEA and HEI than the lean ones. Similarly, the lean solvent samples contain more OZD, HEDDA and HEIA than the rich ones. Thus, it can be clearly stated that OZD, HEIA and HEEDA are products of thermal degradation (TDP) and HEA and HEI are products of oxidative degradation (ODP).

As shown in Figure 2, the amount of TDP is several dozen percent higher in lean solvent than in the rich one. It is believed that the reason for this is a partial decomposition of TDP or their reaction to other compounds in the oxidizing environment of the absorption column. It is also visible that TDP are formed from the very beginning of the process (first samples were taken 24 hours after the installation was started).

The obtained results show that HEEDA is the most susceptible product of thermal degradation to reactions in the oxidizing environment. HEEDA content varies significantly between the rich and lean solvent samples. In contrast, OZD and HEIA concentrations change less. It may result from the structure of the tested degradation products. HEEDA is an aliphatic amine while both OZD and HEIA are cyclic amines that are more resistant to oxidizing reactions.

Among ODP, less volatile compounds, i.e. ethanolamine derivatives such as HEA and HEI, were identified. Typical products of oxidative degra-

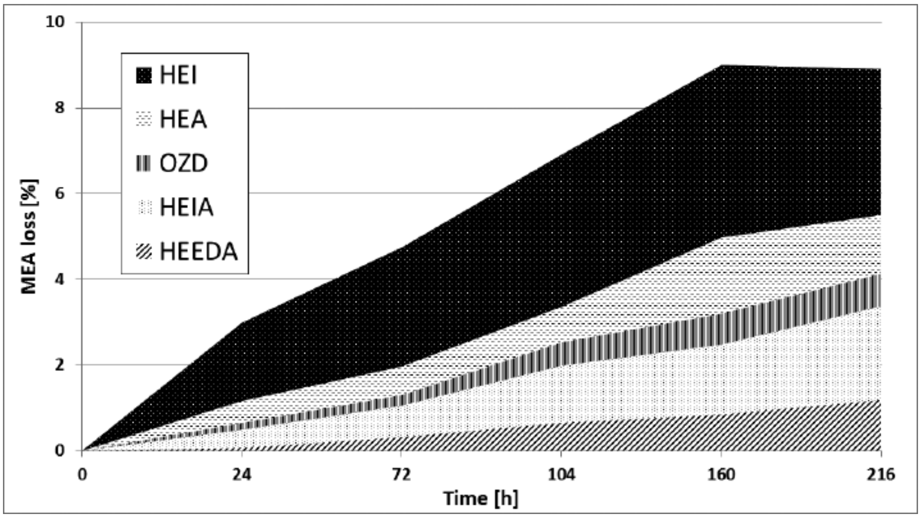


Figure 4.
The calculated loss of MEA in the lean solvent (in the desorber)

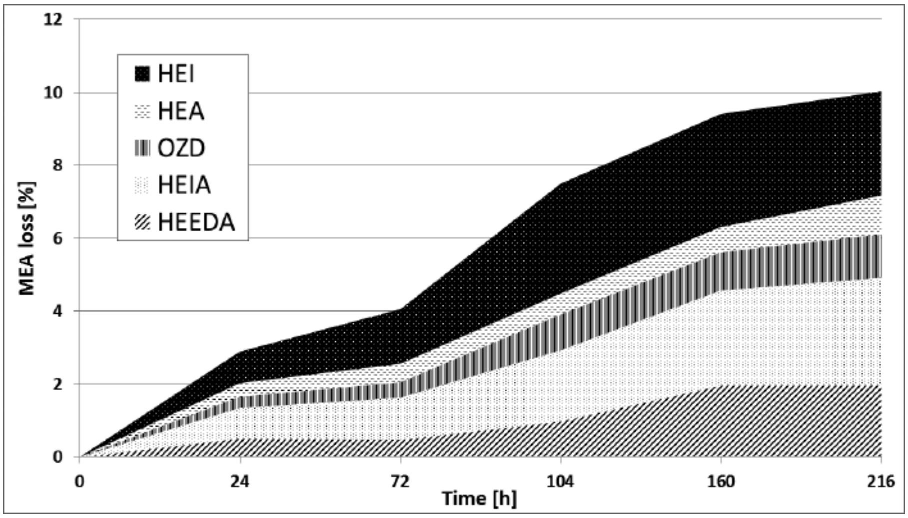


Figure 5.
The calculated loss of MEA in the rich solvent (in the absorber)

dation, e.g. ammonia or carboxylic acids, are largely removed from the system in the regenerator due to their high volatility. Therefore, analysis of this product in the amine solution would be burdened with high error.

Fig. 3 presents the concentrations of ODP in the rich and lean solvent samples. As can be seen, despite the higher initial concentrations of ODP than TDP, the growth of ODP was lower than other degradation products. Thus, it can be concluded that the rich solvent shows clearly less susceptibility to oxidative than to thermal degradation. It can be assumed that the decrease in the concentration of oxidative degradation products in the desorber is caused by the conversion to TDP or the formation of other high-molecular compounds.

Based on the change in the concentration of degradation products over time, the loss of MEA in the solution was estimated. The MEA losses resulting from the formation of individual degradation products are shown in Fig. 4 and Fig. 5. It has been assumed that in the formation of OZD and HEA one amine molecule is involved and in the formation of HEEDA, HEIA and HEI two amine molecules. The initial amine concentration was 4.91 mol/dm^3.

There are few publications presenting research on amine degradation based on samples collected from the CO_2 capture plant, both at lab and pilot scale [37–41]. The data available in the paper [37] (based on pilot studies using 30% MEA) shows that the estimated loss of MEA in the solvent is approx. 1.4 kg/ton of captured CO2 (t_{CO2}), of which 60% is due to thermal degradation and 30% to oxidative degradation. In presented case, the calculated total amine loss was 1.39–1.56 kg MEA/t_{CO2}, of which 39–54% was due to oxidative degradation and 46–61% due to thermal degradation.

Additionally, the data from the publications [40, 42] refer to the amine losses due to oxidative degradation, which amount to 0.29–0.73 kg MEA/t_{CO2}. The results of this paper have shown that the consumption of MEA due to the formation of HEI and HEA (oxidative degradation) was 0.61–0.74 kg MEA/t_{CO2}.

Although the degradation of MEA to ammonia, carboxylic acids, etc. was not taken into account to some extent, the data obtained showed that in the case of CO_2 capture from gases containing both oxygen and elevated carbon dioxide content, degradation is a serious problem. The values of the degree of degradation are so high that it is necessary to use additives that inhibit the degradation process, or to use sorbents alternative to MEA, characterized by increased resistance to degradation processes, to prevent a decrease in the efficiency of CO_2 capture resulting from the reduced amine concentration in the solution.

4. CONCLUSIONS

During these studies, major thermal and oxidative amine degradation products in the amine solvent have been determined by means of gas chromatography. The samples of amine were collected from the laboratory stand used for CO_2 capture from synthetic flue gas containing 30 vol.% of CO_2 (and air). A 30% wt. aqueous solution of MEA was used as a solvent.

The lean amine samples contained more OZD, HEDDA and HEIA than rich amine samples. The rich ones, in turn, included more HEA and HEI. Thus, it has been confirmed that OZD, HEEDA and HEIA are formed due to thermal degradation. By contrast, HEA and HEI are formed by oxidative degradation. Considering the differences in the content of degradation products between rich and lean amine samples it is believed that thermal degradation products undergo reaction to other compounds.

Degradation products were detected after only 24 hours of installation operation and increased over time. Nevertheless, the growth of oxidative degradation products was lower than thermal ones. Therefore, it can be concluded that rich amine is less susceptible to oxidative degradation than the thermal degradation.

After 216 hours the total content of degradation products was in the range of 0.029–0.084 mol/dm^3. Taking into account the obtained results, it has been calculated that the loss of MEA (due to the degradation) was in the range 1.4–1.6 kg MEA/t CO_2, of which thermal degradation was responsible for up to 61% weight loss. This data is comparable with the literature (about 1.4 kg MEA/t CO_2).

Obtained results have shown that in the case of CO_2 capture from gases containing both oxygen and high CO_2 concentration, degradation is a serious problem [44]. Determining the concentration of the degradation products and the rate of their formation is important for evaluating the viability of the solution. Furthermore, it can be helpful in respecting environmental standards.

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