

A shortcut method with guided removal of degradation products and

improved solvent performance for CO₂ capture process

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ABSTRACT

With the post-combustion CO₂ capture process running for a long time, the degradation of aqueous amine-based is inevitable. Unfortunately, a simple and effective way to increase the economic feasibility of CO₂ capture process after accumulated degradation products remains absent, and little attention has been paid to the real effect of degradation products on the CO₂ capture performance in aqueous amine solutions. We propose a simple experimental and computational method that can evaluate the performance and regeneration energy of solvent after change. The method can determine key degradation products that affecting the performance of solvent, so as to guide the selective removal of degradation products and improve solvent performance.

Keywords: degradation product; MEA; bubbling reactor; purification; regeneration energy.

1. Introduction

The burning of fossil fuels is one of the major sources of CO₂ emissions ¹⁻³. It is a contributor to global warming, extreme weather, and rising sea levels, which seriously damages the living environment of human beings ⁴⁻⁷. CO₂ capture, utilization and storage (CCUS) technology is a popular strategy to deal with carbon emissions without decreasing fossil fuel usage ⁸⁻¹⁰. Among them, in addition to the problem of high energy consumption in the process of CO₂ capture, another critical problem is the solvent degradation in the long run ¹¹. Although many researchers have studied many additives that inhibit degradation and developed new absorbents that are not easily degraded, degradation in CO₂ capture is inevitable ¹²⁻¹⁵.

As everyone knows, due to heating and oxidation, the running amine solution degrades over time into other chemicals, which are the degradation products of amines ¹⁶. Type of degradation product depends on the composition of the flue gas and whether flue gas desulfurization and denitrification are employed. With accumulate continuously in the solution, when degradation content reaches a certain degree, the performance of the solution will be significantly reduced and the original process operation also cannot meet the process requirements. At present, the most commonly used measure in industrial processes to simply deal with the loss of performance caused by solvent degradation is to supplement solvent and the cost of chemical make-up account for 20% of operating cost ^{17,18}. A small part of industrial processes maintains the stability of solvent performance by adding solvent purification process, such as distillation, ion-exchange resins (IEX) and electrodialysis ¹⁹⁻²⁴. However, due to the technical limitations and financial investment of the purification process, it is rarely used. Therefore, it is necessary to develop purification technology and how to reduce the cost of purification.

The previous method of purification was to reduce the degraded MEA solution to the original solution as much as possible without considering the specific impact of the degraded product on the solution and whether removing it was the optimal solution. Considering that part degradation products may have little effect on solution performance and may even enhance solution performance, it is necessary to establish a method to evaluate the effect of degradation products on solution performance and regeneration energy. Through a method as a guide, effective degradation products can be selectively retained to enhance solvent performance, and adverse degradation products will be targeted for removal, thus achieving the effect of reducing the separation difficulty and cost.

As the benchmark solution, monoethanolamine (MEA) solution is undoubtedly the most widely studied and applied solvent, and novel solvent studies are inseparable from the MEA solution for comparison ²⁵. MEA has a wide range of degradation products and common degradation products during the absorption of CO₂ by MEA aqueous solution in post-combustion capture after flue gas desulfurization and denitrification are formic acid (FA), formamide (FM), acetamide (AM), ethylamine (EA), 2-methylpiperazine (2MPZ), 2-(methylamino) ethanol (2MAE), 1-amino-2-propanol (1A2P), N-(2-hydroxyethyl) piperazine (N2HEPZ), N-(2-hydroxyethyl) ethylenediamine (N2HEEDA), 3-picoline (3PC), imidazole (IA), 2-oxazolidinone (2OZ) and N-methylmorpholine (NMM) ²⁶⁻²⁸. In addition, the degradation in the process of CO₂ capture by organic amine solution conforms to a unified law, that is, the degradation process is first slow and then fast. When a certain degradation substance reaches a certain amount of accumulation, the catalytic effect on the degradation process may occur, and the degradation process will grow exponentially. Therefore, in this work, 5mol/LMEA and 0.5mol/L degradation products were selected as the research objects. The rapid reaction experiment was carried out through the fast bubbling reactor, and the calculation method of regeneration energy was established based on the fast bubbling reaction device and data, so as to realize the purpose of analyzing and guiding the performance of amine solutions containing different single degradation products.

2. Experimental Methods and Theories

2.1. Materials

MEA (99 wt%, AR), formic acid (99%), formamide (99%, AR), acetamide (99%, AR), ethylamine (68-72%, in H₂O), 2-methylpiperazine (98%), 2-(methylamino) ethanol (99%), 1-amino-2-propanol (> 93%, GC), N-(2-hydroxyethyl) piperazine (98%), N-(2-hydroxyethyl) ethylenediamine (99%), 3-picoline (99%), imidazole (99%), 2-oxazolidinone (99%) and N-methylmorpholine (> 99%,GC) were purchased from Aladdin Industrial Corporation, Shanghai, China. CO₂ (99.9%) and N₂ (99.99%) was supplied by Changsha Rizhen Gas Co. Ltd., China.

2.1.1 Experimental Solution

Various experimental solutions were prepared in turn. In this work, it is assumed that the concentration of degradation product produced by MEA degradation is 0.5mol/L. The concentration of 5.5 mol/L aqueous MEA solution was regarded as pre-degradation solution. Aqueous solutions consisting of 5mol/L MEA and 0.5mol/L degradation products is considered as a post-degradation solution (or pre-purification solution). Assuming that various degradation product can be completely removed from aqueous MEA solution, the post-purification solution will be a 5mol/L aqueous MEA solution.

2.2. Absorption and Desorption Process

Figure S1 shows the fast bubbling reaction device during the CO₂ absorption and desorption process used in this work. The device was mainly composed of air inlet cylinder, gas mass

flowmeter, three-port reactor, water bath, condensing tube, infrared analyzer and computer. During the absorption process, the mixed gases of CO₂ and N₂ enter the three-port reactor from the left port. After the bubbler, CO₂ reacts quickly with aqueous amine solution. The gas after the reaction flows through the condensation and drying process and was detected by the infrared analyzer, whose detection results were recorded in real time on the computer. The desorption process is the same as the absorption process, but only N₂ enters the reactor. N₂ can dilute the CO₂ released by the aqueous amine solution and be detected by the infrared analyzer. The conditions of absorption and desorption process can be obtained from **Table 1**. A more specific process can be found in **Support Information**.

Table 1. Experimental conditions of absorption and desorption.

Items	Absorption process	Desorption process
Experimental temperature	40 °C	80 °C
Start temperature	40 °C	70 °C
Gas flow	150/850 mL/min (CO ₂ /N ₂)	850 mL/min (N ₂)
Liquid V	300 mL	300 mL
Stirring rate	1300 r/min	1300 r/min

2.2.1 Absorption and Desorption Rate

Based on the constant gas flow rate of N₂ in the whole process, combined with the dynamic CO₂ detection results of the infrared analyzer, the amount of CO₂ absorbed into or released from aqueous amine solution per unit time can be obtained.

$$n_{CO_2} = \frac{G_{N_2}}{V_m} \left| \frac{x_{i'}}{1-x_{i'}} - \frac{x_{out}}{1-x_{out}} \right|$$

(1)

where n_{CO_2} (mol/s) is the amount of CO_2 absorbed into or released from the solution; G_{N_2} (L/min) is the flow rate of N_2 ; V_m is the molar volume of the gas; x_i and x_{out} (mol/(s·L)) are the import and export concentrations of CO_2 , respectively. It should be noted that the real gas temperature needs to be corrected when formula (1) is used for calculation.

The absorption rate and desorption rate can be obtained by amount of CO_2 absorbed or released per unit time dividing the volume of solution.

$$r_{CO_2} = \frac{n_{CO_2}}{V}$$

(2)

where r_{CO_2} (mol/(L·s)) is absorption rate or desorption rate of CO_2 into or out solution; V (L) is the volume of the solution.

The average CO_2 absorption and desorption rates can be obtained by integration.

$$\bar{r}_{CO_2} = \frac{\int_0^t n_{CO_2} dt}{Vt}$$

(3)

Relative average rate was used to evaluate the effect of degradation products on absorption rate and reaction rate of aqueous amine solution after and before degradation or purification.

$$RD = \frac{\bar{r}_{CO_2, post-degradation}}{\bar{r}_{CO_2, pre-degradation}}$$

$$RP = \frac{\bar{r}_{CO_2, post-purification}}{\bar{r}_{CO_2, pre-purification}}$$

(4)

where RD and RP are the relative average rate after and before degradation, and the relative average rate after and before purification, respectively.

2.2.2 Solution CO₂ Capacity

The accumulation of the amount of CO₂ absorbed per unit time by amine solution is the absorption loading, and the rich solution loading minus the amount of CO₂ released per unit time by amine solution is the desorption loading.

$$a_{abs} = \frac{\int_0^t n_{CO_2} dt}{V}$$

$$a_{des} = a_{rich} - \frac{\int_0^t n_{CO_2} dt}{V}$$
(5)

where a_{abs} and a_{des} (mol/L) are the CO₂ loadings in the solution after absorption and desorption.

The absorption and desorption amount of CO₂ in liquid phase can be calculated as follows:

$$a = \alpha C_{am}$$
(6)

where a (mol/L) and α (mol/mol) are both the CO₂ loadings in the solution; C_{am} (mol/L) is the concentration of amine in solution.

2.2.3 Solution Cyclic Utilization Rate

The degree of CO₂ absorption and release in solvents determines the circulation capacity in the single absorption and desorption process, so the cyclic CO₂ capacity is related to the loading of rich and lean solvent.

$$a_{cyc} = a_{rich} - a_{lean} \quad (7)$$

where a_{cyc} (mol/L) is cyclic CO₂ capacity; a_{rich} and a_{lean} (mol/L) are the CO₂ loadings in rich solution and lean solution.

In this work, solution cyclic utilization rate V_{cyc} (m³/t CO₂) was defined as the required solution volume of the circulation solution per ton of CO₂ product.

$$V_{cyc} = \frac{N_{CO_2}}{a_{cyc}} \quad (8)$$

where N_{CO_2} is the mol of CO₂ for 1 ton, approximate 2.2722×10^4 mol.

2.2.4 Regeneration Energy

The regenerated energy in the desorption process is generally divided into three parts: reaction heat (the heat required for CO₂ desorption reaction), sensible heat (the heat required for temperature rise of solution) and latent heat (the heat required for evaporation of solution)²⁹. The equations for regeneration energy consumption can be derived from the energy balance in the reactor desorption process as shown in **Figure S1**, and the conditions of desorption process can be found from **Table 1**. Since the highest temperature in the whole desorption process is 80°C, without water vapor and no

latent heat will be generated in this process, so the equation of regeneration energy can be written as follows.

$$Q_{regen} = Q_{reac} + Q_{sens} \quad (9)$$

Based on one absorption-desorption process carried out by the device in **Figure S1**, some basic assumptions are required to calculate the regeneration energy: 1) No water vapor to be produced during desorption and no water is taken away. 2) Constant temperature and N₂ flow in the reactor. 3) The release of 1 ton of CO₂ gas is caused by the multiple superpositions of the absorption-desorption process. 4) Heat capacity of a mixture is molar-weighted average value of pure species, and a species has the same heat capacity regardless of the gas phase and the liquid phase. 5) Ideal and actual conditions do not affect the calculation of Q_{regen} .

$$Q_{regen} = Q_{reac,2} + Q_{sens,2} - Q_{reac,1} - Q_{sens,1}$$

$$Q_{sens,1} = V_{cyc} (C_{am} c_{am} + C_w c_w + C_d c_d + a_{rich} c_{CO_2}) (T_1 - T_0)$$

$$Q_{sens,2} = V_{cyc} (C_{am} c_{am} + C_w c_w + C_d c_d + a_{lean} c_{CO_2}) (T_2 - T_0) + N_{CO_2} c_{CO_2} (T_2 - T_0)$$

$$Q_{reac,1} = -C_{am} V_{cyc} \int_0^{\alpha_{rich}} \Delta H_{l|d}(\alpha) d\alpha$$

$$Q_{reac,2} = -C_{am} V_{cyc} \int_0^{\alpha_{lean}} \Delta H_{l|d}(\alpha) d\alpha$$

$$(10)$$

Substituting of equation (10) into equation (9) gets the following:

$$Q_{regen} = V_{cyc} (C_{am} c_{am} + C_w c_w + C_d c_d + a_{lean} c_{CO_2}) (T_2 - T_1) + N_{CO_2} c_{CO_2} (T_2 - T_1) - C_{am} V_{cyc} \int_{\alpha_{lean}}^{\alpha_{rich}} \Delta H_{|i|} d\alpha \quad (11)$$

where Q_{regen} , Q_{reac} , and Q_{sens} (GJ/t CO₂) represent the total regenerated heat, reaction heat, and sensible heat, respectively. C_{am} , C_w and C_d are the concentration of amine, water and degradation products, respectively. c_{am} , c_w , c_d and c_{CO_2} (kJ/(mol·K)) are the heat capacity of amine, water, degradation products and CO₂, respectively. $\Delta H_{|i|}$ (kJ/mol) is absorption heat of CO₂. T_0 , T_1 and T_2 (°C) are the room temperature, start temperature and desorption temperature.

The value of $\Delta H_{|i|}$ can be obtained by combining the Gibbs-Helmholtz equation with the VLE data.

$$-\Delta \frac{H_{|i|}}{R} = \left[\frac{d(\ln p_{CO_2}^i)}{d\left(\frac{1}{T}\right)} \right]_{\alpha} \quad (12)$$

where $p_{CO_2}^i(T, \alpha)$ is the rich CO₂ partial pressure.

3. Results and Discussion

3.1. Reliability of Data

In this work, the reliability of the experimental apparatus is verified by the principle of CO₂ mass balance in gas and liquid phase. The gas phase CO₂ was measured by the infrared analyzer as shown in **Figure 1S** and the liquid phase CO₂ was determined by titration method as shown in **Figure S2**. The average absolute relative deviation (AARD) between the amount of CO₂ determined

by the gas phase infrared analyzer and the liquid phase titration only was 1.59%. It was indicating that the experimental device and data are reliable.

3.2. CO₂ Absorption Performance

The dynamic state of solution CO₂ loading and absorption rate in the process of CO₂ absorption were investigated by the fast bubbling absorption method. According to the results of the absorption process that were shown in **Figure 1**, the role of degradation products in the process of MEA solution absorption can be preliminarily analyzed. From the overall trend, the CO₂ loading of the solutions first increases gradually, and then tends to be flat and stable at a certain value. The absorption rate decreases slowly at first, then intensifies to decrease, and finally tends to be stable (close to 0). The main absorption capacity of the CO₂ absorption process is reflected in the first 150 minutes. In terms of the comparison among the solutions, the production of degradation products can obviously cause the up or down translation of CO₂ loading curve and absorption rate curve. In order to easier understand the effect of degradation products on the CO₂ absorption performance of solution before and after degradation and purification, the following part further extracts and analyzes the relevant data of the absorption process.

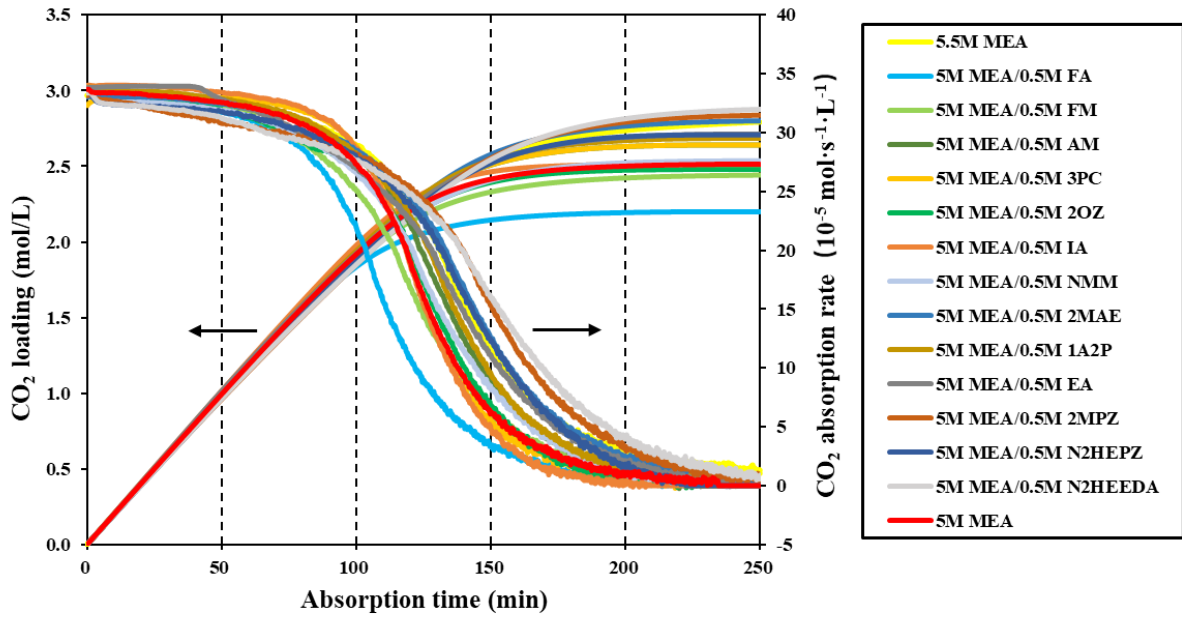


Figure 1. Curves of CO₂ loading and absorption rate with time in the absorption process of 5M MEA, 5.5M MEA and 5M MEA/0.5M degradation products at 40 °C and a CO₂ partial pressure of 15 kPa.

3.1.1 Absorption Capacity

Demonstrations from the **Figure 1** that the CO₂ loading for the various solution becomes basically near-saturated due to enough absorption time during experimental process. So, the rich CO₂ loading of various solution for absorption time of 150 min was obtained and shown in **Figure 2**. It is interesting to note that the rich CO₂ loading was divided into three regions to discuss depending upon the discrepancy of various solution in **Figure 2**: within region I and III only the pre-degradation and post-purification solution, which concentration are 5.5 mol/L and 5 mol/L aqueous MEA solution, and in region II are thirteen post-degradation solution (i.e. pre-purification solution) with a mixture concentration of 5 mol/L MEA and 0.5 mol/L degradation products. Region I with II demonstrates

the changes in rich CO₂ loading before and after solution degradation. Before aqueous MEA solution degradation, the rich CO₂ loading value is 2.79 mol/L, while some rich CO₂ loading values increase and decrease after the introduction of degradation products (post-degradation) in aqueous MEA solution with the order of 5M MEA/0.5M N2HEEDA (2.88) > 5M MEA/0.5M 2MPZ (2.84) > 5M MEA/0.5M 2MAE (2.80) > 5.5M MEA (2.79) > 5M MEA/0.5M EA (2.71) = 5M MEA/0.5M N2HEPZ (2.71) > 5M MEA/0.5M 1A2P (2.68) > 5M MEA/0.5M AM (2.64) > 5M MEA/0.5M NMM (2.54) > 5M MEA/0.5M 3PC (2.53) > 5M MEA/0.5M IA (2.51) > 5M MEA/0.5M 2OZ (2.48) > 5M MEA/0.5M FM (2.44) > 5M MEA/0.5M FA (2.19). That is, the rich CO₂ loading could be declined from 2.84% to 21.43% with the addition of various degradation products, such as EA, N2HEPZ, 1A2P, AM, NMM, 3PC, IA, 2OZ, FM and FA, while the rich CO₂ loading could be improved by 0.29% to 3.00% when the 2MAE, 2MPZ and N2HEEDA were introduced into solution. Accordingly, the introduction of most degradation products could decrease the solution capacity for CO₂ and only a small proportion of degradation could enhance rich capacity for solution, and FA presented the worst result on rich CO₂ loading in solution.

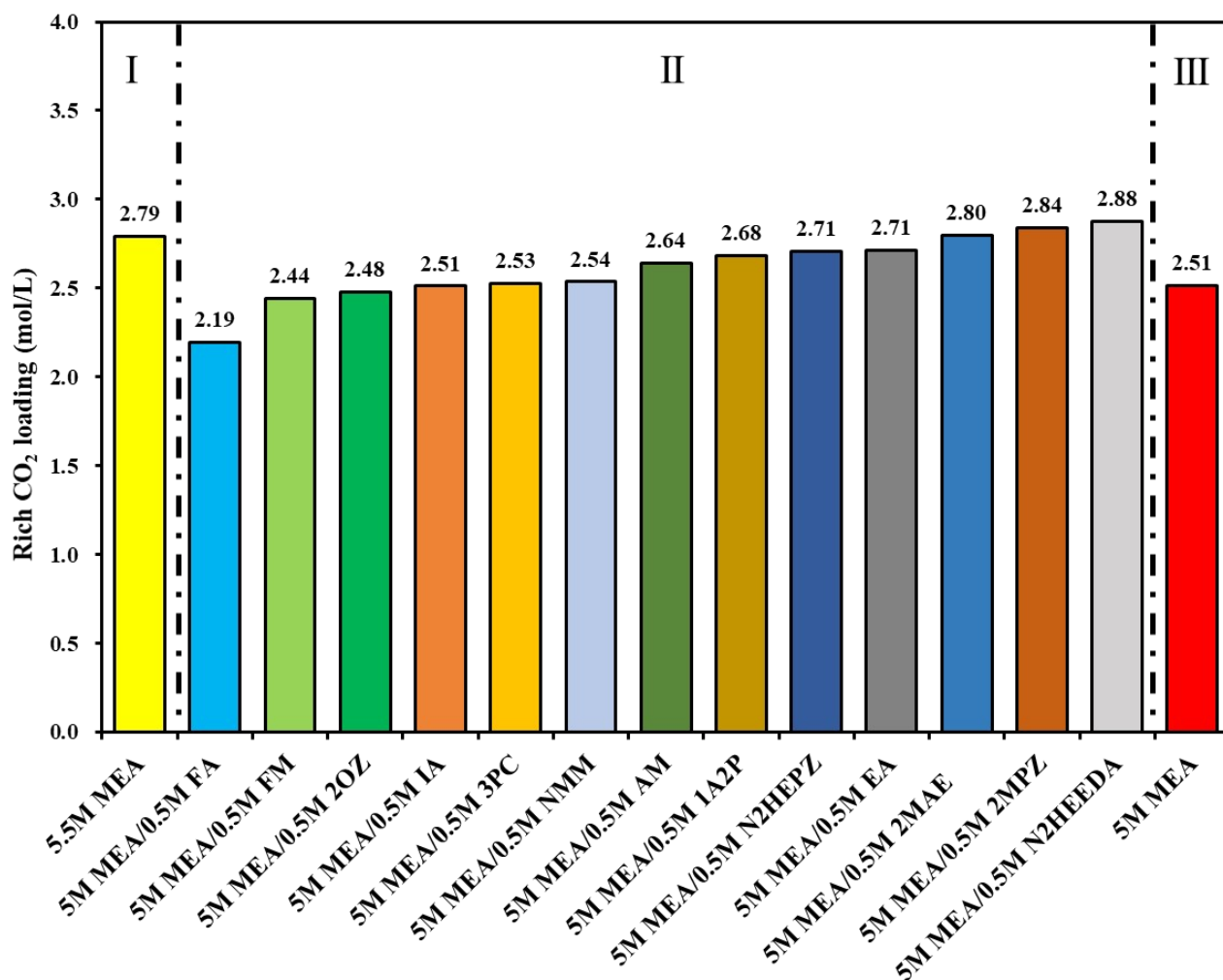
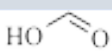


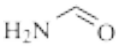
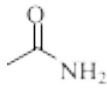
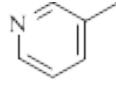
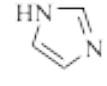
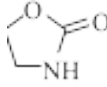
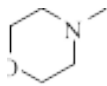
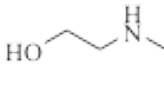
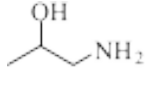
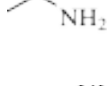
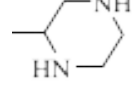
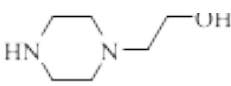
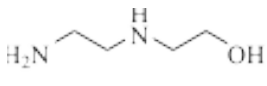
Figure 2. Rich CO₂ loading of 5.5M MEA, 5M MEA/0.5M degradation products and 5M MEA at 40 °C and a CO₂ partial pressure of 15 kPa (region I pre-degradation solution, region II post-degradation solution, and region III post-purification solution).

The rich CO₂ loading is symbolized the CO₂ absorption capacity for solution, which determined by property of solution themselves. Original aqueous MEA solution can absorb CO₂ is due to MEA can react with CO₂ to form heat-unstable carbamate. When 5.5M MEA (pre-degradation solution) became to 5M MEA (post-purification solution), shown in **Figure 2**, the CO₂ absorption capacity bring down 9.98% because of the decreasing active ingredients in solution. So, the decisive factor is that degradation product property to lead to the rich CO₂ loading discrepancy for post-degradation

solution. In theory, if degradation product can react with CO₂ among the post-degradation solution, the rich CO₂ loading would be no significantly rise or fall, such as 5M MEA/0.5M AM, 5M MEA/0.5M 1A2P, 5M MEA/0.5M N2HEPZ, 5M MEA/0.5M EA, 5M MEA/0.5M 2MAE, 5M MEA/0.5M 2MPZ and 5M MEA/0.5M N2HEEDA, which rich CO₂ loading values change within 5.00% contrasted to pre-degradation solution. If degradation products have not active for CO₂, only 5M MEA active ingredient in post-degradation solution, which absorption capacity was similar post-purification solution, the rich CO₂ loading values decreasing approximately 10.00% compared to pre-degradation solution, such as 5M MEA/0.5M FM, 5M MEA/0.5M 2OZ, 5M MEA/0.5M IA, 5M MEA/0.5M 3PC and 5M MEA/0.5M NMM. If degradation product not only cannot react with CO₂, but also can react with MEA in post-degradation solution, the rich CO₂ loading would be significantly reduced by more than 20.00% comparing with pre-degradation solution, such as 5M MEA/0.5M FA. Various degradation products were tabulated in **Table 2**, where the structure and possible reactional equations can be found. Based on the structural characteristics of various degradation product, the types of degradation products could be preliminarily divided into four categories: organic acids (HSSs), amides, nitrogen heterocyclic compounds and amines. So, without a doubt, only amines can react with CO₂ well, and other products are less likely to react with CO₂ smoothly. Of particular concern, formamide can decomposed becoming the HSSs under alkaline conditions but this reaction process is weak according to the literature^{30,31}.

Table 2. Structures and types of degradation products.

Degradation products	Chemical structure	Possible reactions
Formic acid (FA)		$RCOOH + RNH_2 \rightarrow RNH_3^{+} + RCOO^{-}$

Formamide (FM)		$OH^{-} + H_2NCHO \leftrightarrow HCOO^{-} + NH_3$ (weak)
Acetamide (AM)		$2 CH_3CONH_2 + CO_2 \leftrightarrow CH_3CONHCOO^{-} + CH_3CONH_3^{+}$
3-Picoline (3PC)		-
Imidazole (IA)		-
2-Oxazolidinone (2OZ)		-
N-Methylmorpholine (NMM)		-
2-(Methylamino) ethanol (2MAE)		$2 RR'NH + CO_2 \leftrightarrow RR'NCOO^{-} + RR'NH_2^{+}$
1-Amino-2-propanol (1A2P)		$2 RNH_2 + CO_2 \leftrightarrow RNHCOO^{-} + RNH_3^{+}$
Ethylamine (EA)		$2 RNH_2 + CO_2 \leftrightarrow RNHCOO^{-} + RNH_3^{+}$
2-methylpiperazine (2MPZ)		$2 RR'NH + CO_2 \leftrightarrow RR'NCOO^{-} + RR'NH_2^{+}$
N-(2-hydroxyethyl) piperazine (N2HEPZ)		$2 RR'NH + CO_2 \leftrightarrow RR'NCOO^{-} + RR'NH_2^{+}$
N-(2-hydroxyethyl) ethylenediamine (N2HEEDA)		$2 RNH_2 + CO_2 \leftrightarrow RNHCOO^{-} + RNH_3^{+}$ $2 RR'NH + CO_2 \leftrightarrow RR'NCOO^{-} + RR'NH_2^{+}$

3.1.2 Absorption Rate

To further study the effect of degradation product on solution absorption process, the average CO₂ absorption rates with above mentioned various solution for absorption time of 150 min were investigated, and the results were displayed in **Figure 3**. The relative average absorption rate of solution with thirteen different post-degradation solution and pre-degradation solution were

demonstrated in **Figure 3(b)**. The order of the RD (%) is: 5M MEA/0.5M 2MAE (100.8) > 5.5M MEA (100.0) > 5M MEA/0.5M 2MPZ (99.8) > 5M MEA/0.5M N2HEEDA (99.5) > 5M MEA/0.5M 1A2P (99.3) > 5M MEA/0.5M EA (98.8) > 5M MEA/0.5M N2HEPZ (98.5) > 5M MEA/0.5M AM (98.1) > 5M MEA/0.5M IA (96.3) > 5M MEA/0.5M 3PC (95.4) > 5M MEA/0.5M NMM (94.0) > 5M MEA/0.5M 2OZ (93.6) > 5M MEA/0.5M FM (91.1) > 5M MEA/0.5M FA (83.9). One can note that, by contrast pre-degradation solution to post-degradation solution, in addition to FA the average CO₂ absorption rate doesn't change significantly with the introduction of most degradation products. Moreover, the relative average absorption rate of solution with thirteen different post-purification solution and pre-purification solution were displayed in **Figure 3(c)**. The order of the RP (%) is: 5M MEA/0.5M FA (112.6) > 5M MEA/0.5M FM (103.6) > 5M MEA/0.5M 2OZ (100.9) > 5M MEA/0.5M NMM (100.4) > 5M MEA (100.0) > 5M MEA/0.5M 3PC (98.9) > 5M MEA/0.5M IA (98.0) > 5M MEA/0.5M AM (96.2) > 5M MEA/0.5M N2HEPZ (95.8) > 5M MEA/0.5M EA (95.5) > 5M MEA/0.5M 1A2P (95.1) > 5M MEA/0.5M N2HEEDA (94.9) > 5M MEA/0.5M 2MPZ (93.7). The results indicating that removal FA can enhance CO₂ absorption rate of after degradation solution to some extent. The removal of other degradation products did little to increase the absorption rate of the solution.

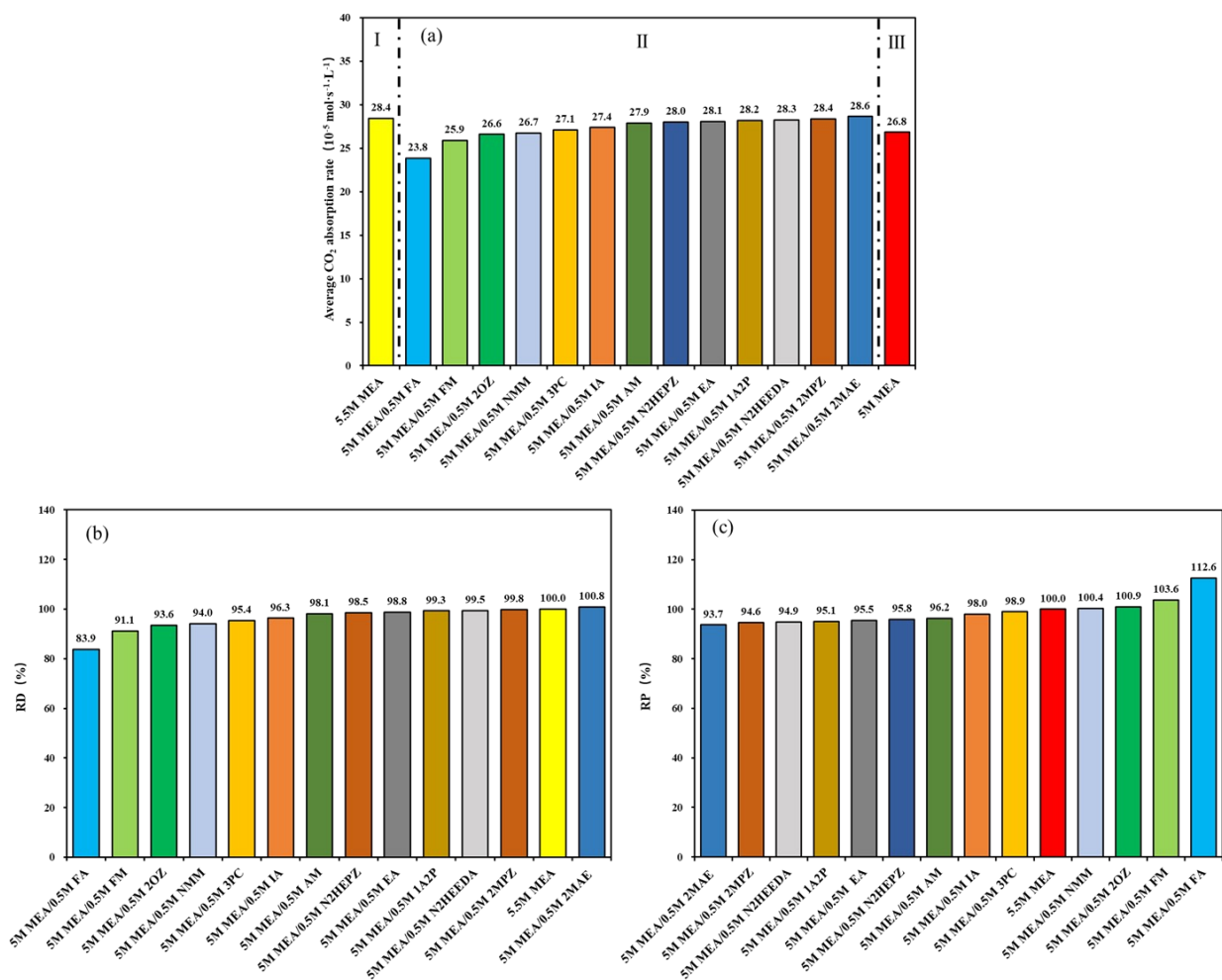


Figure 3. Average CO₂ absorption rate with various solution with absorption time of 150 min at 40 °C and a CO₂ partial pressure of 15 kPa. (a) Average CO₂ absorption rate (region I pre-degradation solution, region II post-degradation solution, and region III post-purification solution). (b) Relative average absorption rate after and before degradation. (c) Relative average absorption rate after and before purification.

3.2. CO₂ Desorption Performance

The dynamic state of solution CO₂ loading and desorption rate with time by the fast bubbling reactor were presented in **Figure 4**. It is note that CO₂ loading of various solution continuously

decrease with desorption time, and its downward trend is first fast and then slow. The desorption rate of CO₂ basically drops to a small value in the 50 minutes, suggesting that desorption rate is primarily focus on the first 50 minutes, and it is most common that the desorption rates were enhance to some degree compared after degradation solution to before degradation solution.

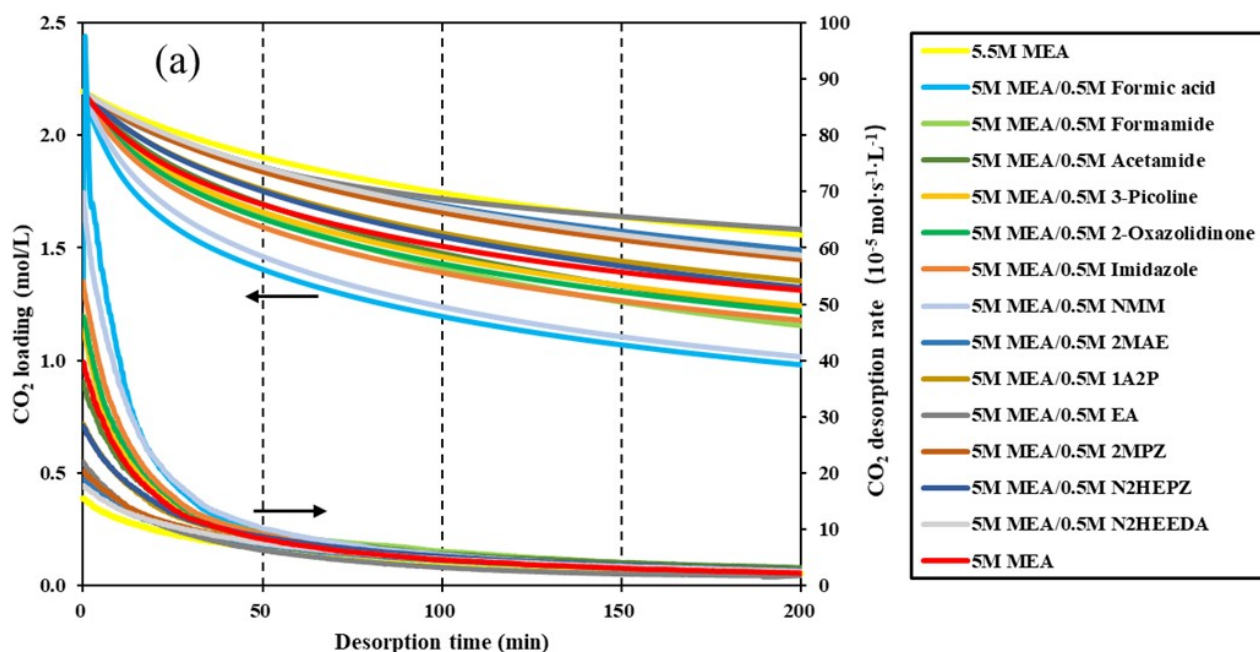


Figure 4. Curves of CO₂ loading and desorption rate with time in the desorption process of 5M MEA, 5.5M MEA and 5M MEA/0.5M degradation products at 80 °C.

3.2.1 Desorption Rate

Average CO₂ desorption rate of various solution with desorption time of 50 min were displayed in **Figure 5**. The results shown that the average CO₂ desorption rate of post-degradation solution general greater than pre-degradation solution. As shown in **Figure 5(b)**, the relative average desorption rate of solution with post-degradation solution to pre-degradation solution were ranked in order as: 5M MEA/0.5M FA (270.6) > 5M MEA/0.5M NMM (251.5) > 5M MEA/0.5M IA (206.6) > 5M MEA/0.5M 2OZ (193.7) > 5M MEA/0.5M FM (188.8) > 5M MEA/0.5M 3PC (183.4) > 5M

MEA/0.5M AM (171.0) > 5M MEA/0.5M N2HEPZ (151.6) > 5M MEA/0.5M 1A2P (149.1) > 5M MEA/0.5M 2MPZ (122.1) > 5M MEA/0.5M EA (116.2) > 5M MEA/0.5M 2MAE (114.9) > 5M MEA/0.5M N2HEEDA (114.8) > 5.5M MEA (100.0). That is to say, the production of degradation products is a benefit to solution desorption process, and especially when the degradation product was FA, NMM and IA, which desorption rate can improve more 2 times.

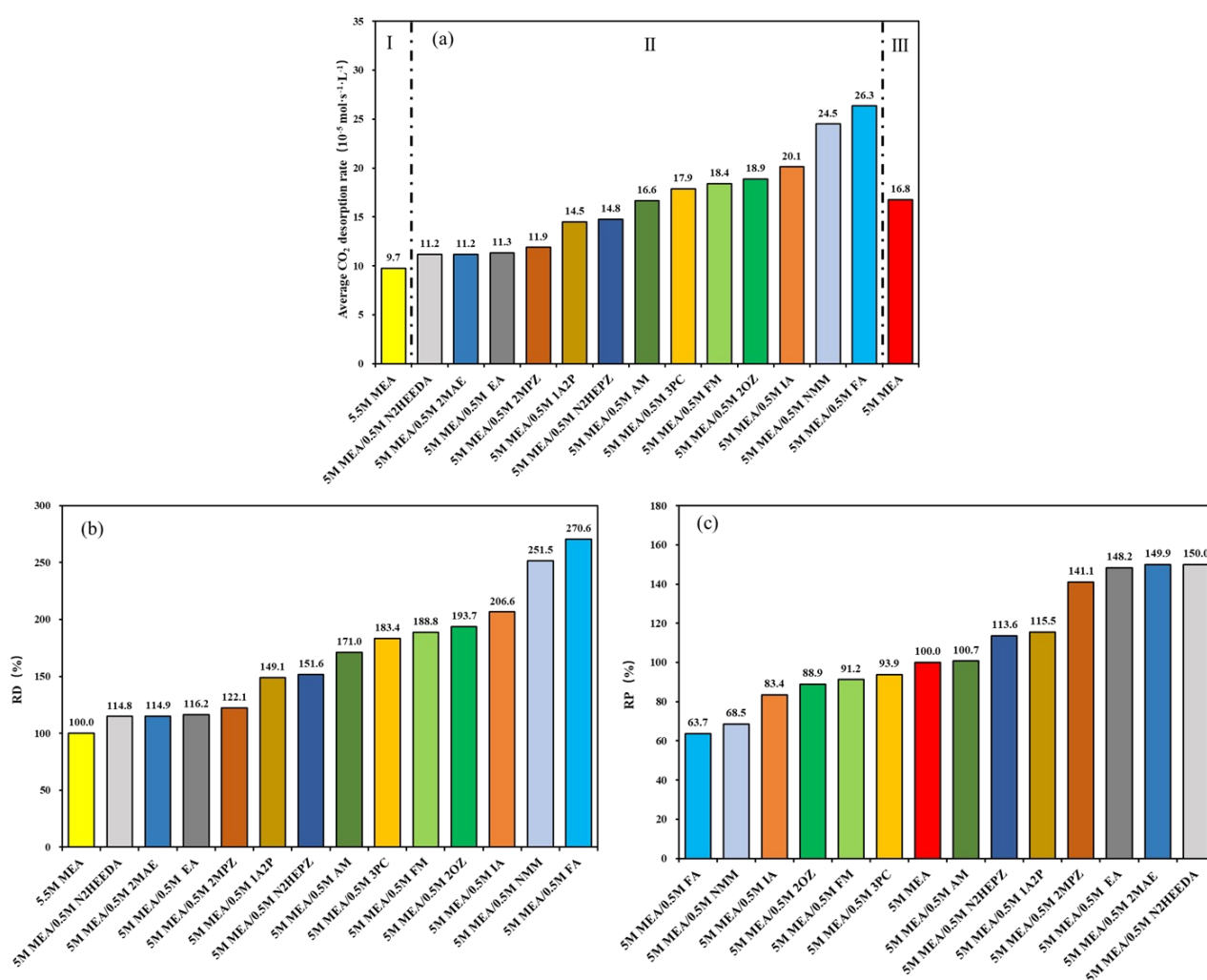


Figure 5. Average CO₂ desorption rate with various solution with desorption time of 50 min at 80 °C. (a) Average CO₂ desorption rate (region I pre-degradation solution, region II post-degradation solution, and region III post-purification solution). (b) Relative average

desorption rate after and before degradation. (c) Relative average desorption rate after and before purification.

The reasons leading to the enhancement of desorption rate for various post-degradation solution could be different. Adding weak acid to MEA solution can make it release CO₂ much faster ³². In addition, E. Jones et al reported a mature phosphorylation technique that the addition of phosphoric acid to MDEA solution significantly improves the hydrogen sulfide removal capacity of regenerators in refinery exhaust gas treatment. It is also pointed out that most heat stable salts are organic acids equivalent to phosphoric acid, which can greatly improve the removal of hydrogen sulfide under appropriate absorption conditions ³³. In this work The production of organic acids that is HSSs could leads to an increase in the concentration of H⁺ in aqueous amine solution, which make the decomposition of carbamates easier at the same temperature ³⁴. Therefore, the addition of FA, FM and AM can promote the desorption rate of post-desorption solution. The mechanism that promoting post-degradation solution desorption with nitrogen-containing heterocyclic compounds (NMM, IA, 2OZ and 3PC) are still unclear and needs further study. Possible reason that post-degradation solution desorption was improved with production of amines is a synergies of mixed amine molecules to extent. In other word, it could be that mixed amines in the same concentration released CO₂ more easily than amines alone.

In addition, the relative average desorption rate of solution with post-purification solution and pre-purification solution were displayed in **Figure 5(c)**. The order of the RP (%) is: 5M MEA/0.5M N2HEEDA (150.0) > 5M MEA/0.5M 2MAE (149.9) > 5M MEA/0.5M EA (148.2) > 5M MEA/0.5M 2MPZ (141.1) > 5M MEA/0.5M 1A2P (115.1) > 5M MEA/0.5M N2HEPZ (113.6) > 5M MEA/0.5M

AM (100.7) > 5M MEA (100.0) > 5M MEA/0.5M 3PC (93.9) > 5M MEA/0.5M FM (91.2) > 5M MEA/0.5M 2OZ (88.9) > 5M MEA/0.5M IA (83.4) > 5M MEA/0.5M NMM (68.5) > 5M MEA/0.5M FA (63.7). That is, when some degradation products such as FA, NMM, IA, 2OZ, FM and 3PC were purified from post-degradation, the desorption rate of post-purification solution would be declined to varying extent. While when the get rid of degradation products from post-degradation are AM, N2HEZ, 1A2P, 2MPZ, EA, 2MAE and N2HEEDA, the desorption rate of post-purification solution would be enhanced to some extent, which meaning that CO₂ bound to aqueous amines with low concentration is more likely to be released.

3.2.2 Solution Cyclic Utilization Rate

Solution cyclic utilization rate, which reference the required solution volume of the circulation solution per ton of CO₂ product, is come from cyclic CO₂ capacity. **Table 3** tabulates the values of lean CO₂ loading, rich CO₂ loading and cyclic CO₂ loading. The effect of various degradation products on solution cyclic utilization rate was studied and the results were demonstrated in **Figure 6**. The order of V_{cyc} (m³/t CO₂) for various solution is: 5M MEA/0.5M FA (28.8) > 5M MEA/0.5M FM (28.5) > 5M MEA (27.7) > 5M MEA/0.5M 2OZ (26.7) > 5M MEA/0.5M EA (26.5) > 5M MEA/0.5M 3PC (26.2) > 5.5M MEA (25.5) > 5M MEA/0.5M IA (24.7) > 5M MEA/0.5M 1A2P (24.6) > 5M MEA/0.5M 2MAE (24.2) > 5M MEA/0.5M AM (24.0) > 5M MEA/0.5M N2HEPZ (23.8) > 5M MEA/0.5M 2MPZ (22.7) > 5M MEA/0.5M N2HEEDA (22.3) > 5M MEA/0.5M NMM (21.2). The smaller the value of solution cyclic utilization rate, the stronger the ability of a solution to absorb CO₂ is, and the less the consumption of a solution to absorb a ton of CO₂ is. Hence, when the

degradation products are IA, 1A2P, 2MAE, AM, N2HEPZ, 2MPZ, N2HEEDA, and NMM in post-degradation solution, the values of solution cyclic utilization rate will be decreases, which is required less solution for the treatment of 1 ton of CO₂. And the values of solution cyclic utilization rate will be increases when the degradation products are FA, FM, 2OZ, EA and 3PC in post-degradation solution, and more solution is needed for the treatment of 1 ton of CO₂. However, after removing the degradation product, only the values of solution cyclic utilization rate for removing FA and FM are reduced, while removal of other degradation products causes to an increase in the amount of solution required to treat 1 ton of CO₂ in solution. In other words, in order to reduce the cost of circulation solution, the degradation products FA and FM should be removed from the solution. In addition, to maintain the solution cyclic utilization rate same between of the post-purification solution and the pre-degradation solution, a fresh MEA must be added to the post-degradation solution to ensure the concentration of MEA in solution.

Table 3. Rich-Lean CO₂ loading of various solution based on the bubbling reactor for desorption time of 50min from 40 °C to 80 °C.

Solution	a_{lean} (mol/L)	a_{rich} (mol/L)	a_{cyc} (mol/L)
5.5M MEA	1.90	2.79	0.89
5M MEA/0.5M FA	1.41	2.19	0.79
5M MEA/0.5M FM	1.64	2.44	0.80
5M MEA/0.5M AM	1.70	2.64	0.95
5M MEA/0.5M 3PC	1.66	2.53	0.87
5M MEA/0.5M 2OZ	1.63	2.48	0.85
5M MEA/0.5M IA	1.59	2.51	0.92
5M MEA/0.5M NMM	1.46	2.54	1.07
5M MEA/0.5M 2MAE	1.86	2.80	0.94
5M MEA/0.5M 1A2P	1.76	2.68	0.92
5M MEA/0.5M EA	1.86	2.71	0.86
5M MEA/0.5M 2MPZ	1.84	2.84	1.00
5M MEA/0.5M N2HEPZ	1.75	2.71	0.95

5M MEA/0.5M N2HEEDA	1.86	2.88	1.02
5M MEA	1.69	2.51	0.82

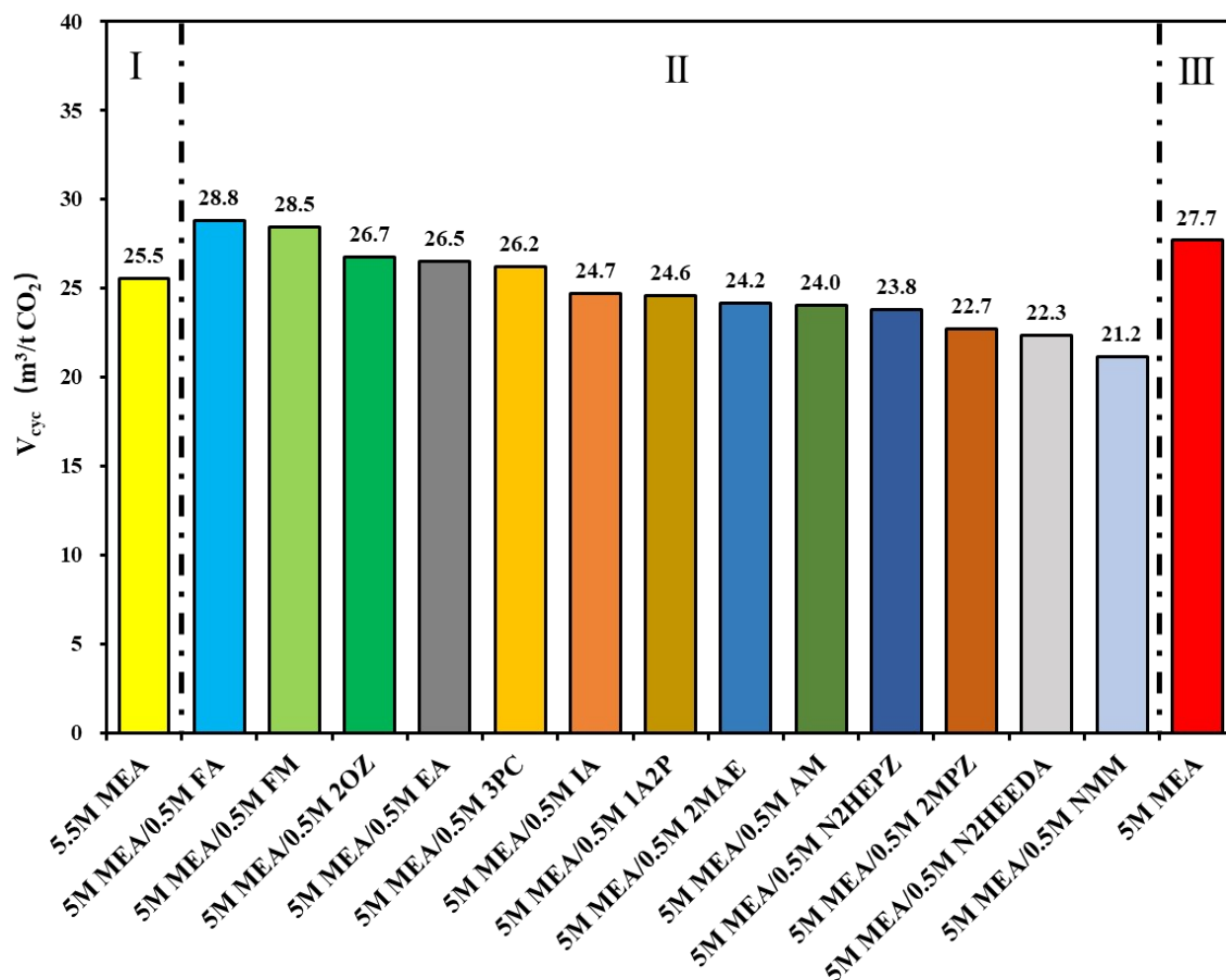


Figure 6. Solution cyclic utilization rate of various solution at absorption temperature of 40 °C and desorption temperature of 80°C within bubbling reactor (region I pre-degradation solution, region II post-degradation solution, and region III post-purification solution).

3.2.3 Regeneration Energy

The heat capacity of various pure species was listed in **Table 4**. Since there is little difference in sensible heat between the maximum heat capacity and the minimum heat capacity in **Table 4**, it is

assumed that the heat capacity of pure 2OZ, IA, NMM, 2MPZ and N2HEPZ are the same as MEA. The absorption heat of CO₂ can be obtained at the same condition from the reported by Inna Kim and Hallvard F. Svendsen³⁵. The effect of various degradation products on solution regeneration energy and the results were displayed in **Figure 7**. The order of Q_{sens} (GJ/t CO₂) for various solution is: 5M MEA/0.5M FA (4.70) > 5M MEA/0.5M FM (4.68) > 5M MEA (4.63) > 5M MEA/0.5M EA (4.42) > 5M MEA/0.5M 2OZ (4.40) > 5.5M MEA (4.36) > 5M MEA/0.5M 3PC (4.29) > 5M MEA/0.5M 1A2P (4.08) > 5M MEA/0.5M IA (4.06) > 5M MEA/0.5M AM (4.05) = 5M MEA/0.5M 2MAE (4.05) > 5M MEA/0.5M N2HEPZ (3.83) > 5M MEA/0.5M 2MPZ (3.77) > 5M MEA/0.5M N2HEEDA (3.76) > 5M MEA/0.5M NMM (3.48). The results showed that the degradation products of FA, FM, EA, 2OZ increased the regeneration energy consumption of the solution after degradation, while the production of other degradation products reduced the regeneration energy consumption, and especially the NMM can reduce the regeneration energy of solution by 20.23%. After removing the degradation products from these solutions, only the removing of FA, FM, EA and 2OZ can reduce the energy consumption of regeneration. Therefore, in MEA aqueous solution, the production of most degradation products is conducive to the reduction of regeneration. In addition, the addition of fresh MEA to the post-purification solution also helps to reduce regeneration energy.

Table 4. The heat capacity of various pure species from 40 to 80 °C

Species	c_p kJ/(mol·K)
MEA	0.1656
FA	0.1019
FM	0.1136
AM	0.1452
3PC	0.1675
2MAE	0.1834
1A2P	0.1988

EA	0.1347
N2HEEDA	0.2506
H ₂ O	0.0755
CO ₂ (g)	0.0385

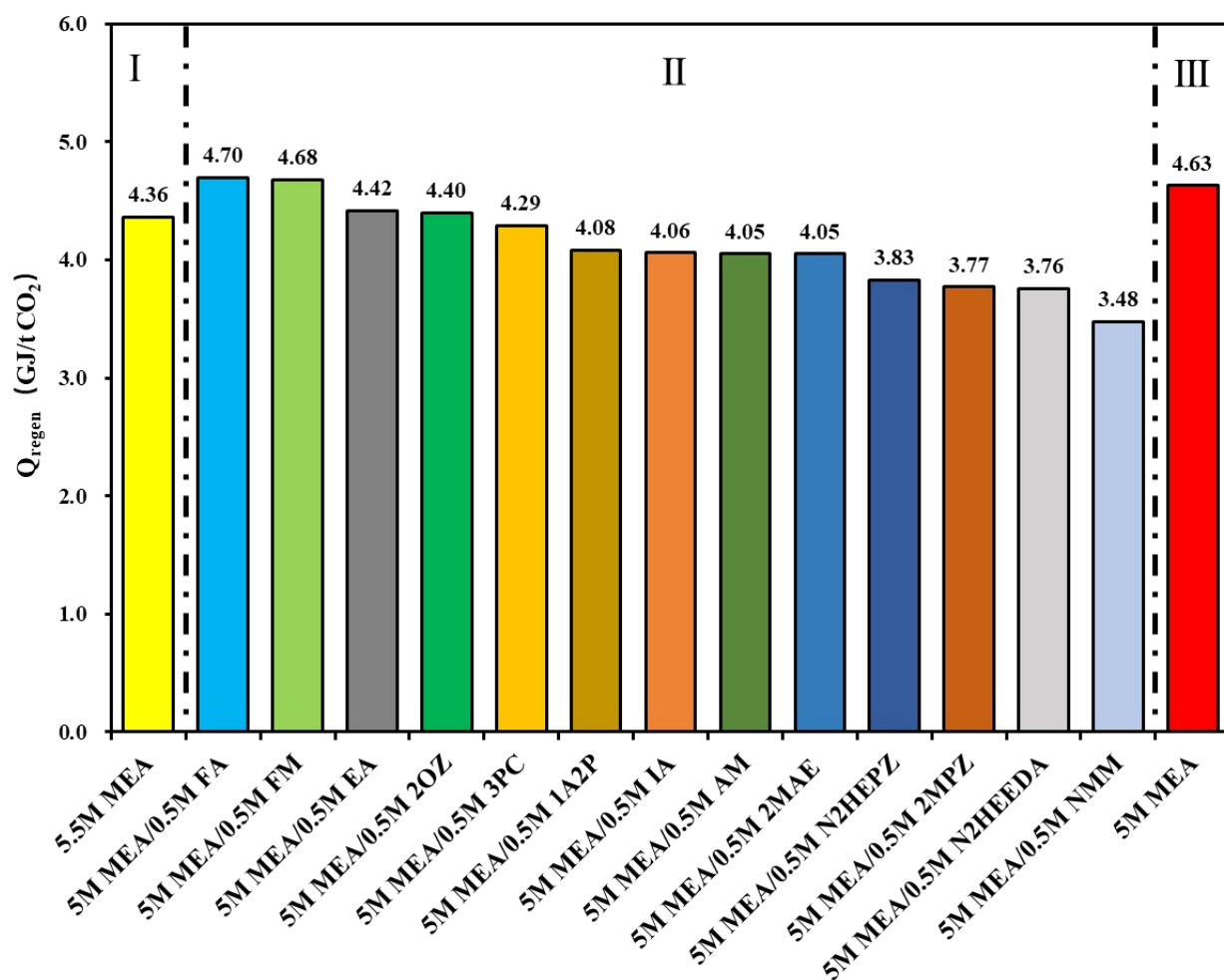


Figure 7. Regeneration Energy of various solution at absorption temperature of 40 °C and desorption temperature of 80°C within bubbling reactor (region I pre-degradation solution, region II post-degradation solution, and region III post-purification solution).

4. Prospect

In the industrial process, the flue gas after desulfurization and denitrification is mainly composed of O_2 , N_2 and CO_2 . Through the absorber, the CO_2 is absorbed by the solvent, and N_2 and O_2 are discharged into the atmosphere. In the presence of O_2 and N_2 , organic acid degradation products are produced under the action of catalytic iron and heat-stable salts are formed in the solution. Thermal degradation and carbamate polymerization occur during the CO_2 release process in the desorption column. With the accumulation of degradation products in the solvent and the loss of the solvent, the long-term operation of the solution in industry results in the deterioration of solvent performance and the increase of regeneration energy consumption. As mentioned above, due to the different effects of degradation products on the absorption and desorption performance of solutions, appropriate measures can be taken to improve the process according to the characteristics of degradation products in order to improve the solution cyclic utilization efficiency in operation and reduce the regeneration energy as demonstration in **Figure 3**. Specific measures are as follows: i) Replenish fresh amine solvent at ⑧ places to make up for the lost solvent, improve absorption performance and regeneration energy consumption; ii) Set up a purification device for removing degradation products FA, FM, EA and 2OZ to improve absorption performance and reduce renewable energy consumption; iii) The presence of the remaining degradation products can reduce the regeneration energy consumption and promote desorption, which can be considered not to be removed. In addition, it is worth noting that in order to promote industrial CO_2 capture and reduce energy consumption, the removal method of degradation products and the mechanism of degradation

products promoting desorption and reducing regeneration energy consumption need to be further studied.

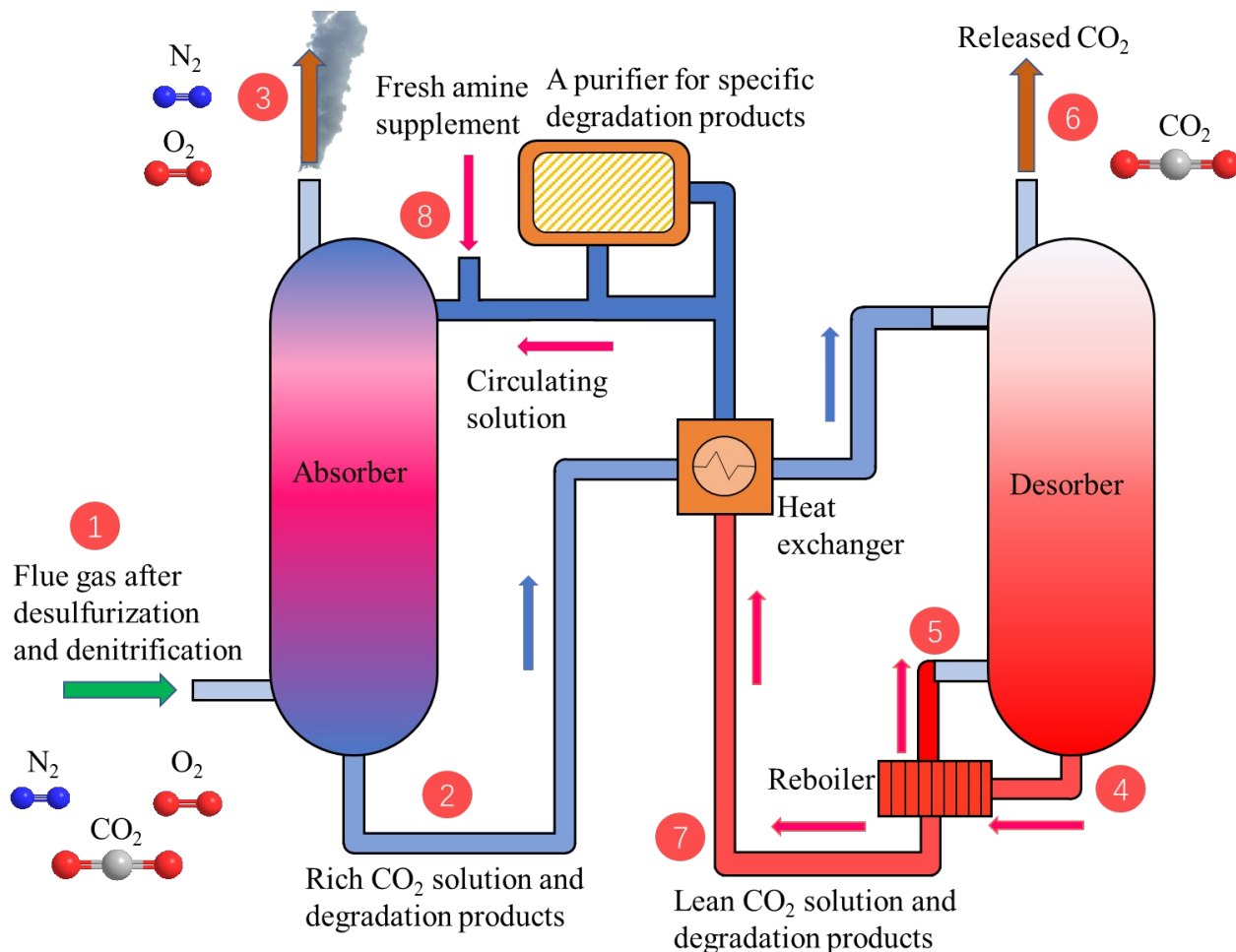


Figure 3. The process of improving the solution circulation performance and reducing energy consumption in the process of capturing CO₂ with amine solution.

5. Conclusions

Base on the absorption and desorption process using in fast bubbling reactor, a simple calculational method was successful developed to evaluate performance and regeneration energy of aqueous MEA solutions accumulating single degradation products. According to the analysis, most

of the degradation products have little influence on the absorption performance, but have great influence on the desorption performance. Degradation to FA, FM, EA, and 2OZ increases the regeneration energy of the solution, which should be removed from the solution in a timely manner in order to improve the performance of the cyclic solution and reduce the regeneration energy consumption. Moreover, timely supplement of amine solvent can not only enhance the absorption and absorption of solvent, but also reduce the regeneration energy.

Using this way, not only guide the maintenance and improvement of the performance of the degraded solution, but also help to guide the research on the purification of the solution, so as to reduce the difficulties in the purification research. In addition, the mechanism of promoting desorption of amine solution by nitrogen heterocyclic compounds such as NMM deserves further study in future.

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Supplementary information

Supplementary information associated with this article can be found in **Supporting Information**.

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