Effects of Alkanolamine Absorbents in Integrated Absorption–Mineralization

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Abstract: Integrated absorption–mineralization (IAM) involves the transformation of CO$_2$ in a chemical-based solution with brine used as the absorbent to form insoluble carbonates and is promising for carbon capture, utilization, and storage. Various types of absorbents such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and aminomethyl propanol (AMP) were examined in multicycle integrated absorption–mineralization (multicycle IAM) involving absorption, precipitation, and regeneration steps between 20 °C and 25 °C at atmospheric pressure in order to reveal their performance in terms of CO$_2$ absorption and conversion and absorbent degradation. We found that 5 wt.% AMP offered 89.5% CO$_2$ absorption capacity per unit of absorbent converted into the amount of solid carbonate within 4 cycles. In addition, it was moderately degraded by 64.02% during the first cycle and then reduced from 30% to 10% in the next cycle (>2 cycles). In comparison with MEA, which was used as the initial absorbent, AMP provided a fivefold increase in the speed of multicycle IAM.

Keywords: absorbent degradation; carbonate; carbon capture, utilization, and storage (CCUS); CO$_2$ absorption capacity; CO$_2$ conversion; multicycle integrated absorption–mineralization (IAM)

1. Introduction

Around 11,000 global-climate-related disasters resulted in over 475,000 deaths and 77% of total economic losses, USD 2.5 trillion, for 160 countries in the previous two decades [1,2]. As the negative consequences of the climate crisis have been widely expanded, the decarbonization has received significant emphasis [3,4]. Carbon dioxide (CO$_2$) emissions are recognized as a major cause of the climate crisis, and those emissions significantly increased in 2021, reaching 36.4 billion metric tons [5–7].

Negative emission technologies have been proposed to remove CO$_2$ emissions from industrial and power plants, which is a sustainable technology to long-term reduce and store CO$_2$. Carbon capture, utilization, and storage (CCUS) is one of the promising techniques that can be deployed to continue commercial feasibility. By capturing CO$_2$ in specified storage facilities, CCUS technology ensures harmful emissions are prohibited from being released into the atmosphere, including economic benefits accrued by applying CO$_2$ [8–11]. According to CO$_2$ capture, various technologies such as physical and chemical absorption, adsorption, and membrane have been developed and supported for the postcombustion capture process [12]. Utilization and storage of CO$_2$ have been demonstrated for extensive applications, both nonconversion and conversion use, approximately 230 metric tons per year [13]. CO$_2$-based building material is one of the pathways for CO$_2$ utilization and storage, which requires low-energy intensity compared with fuel and chemical conversions [8]. As CO$_2$ reacts with minerals or waste products, such as iron slag, to form insoluble carbonates, CO$_2$ gases might be permanently stored and supplied as a feedstock [14–16].

There are two representative approaches to convert CO$_2$ into carbonate: direct and indirect [17]. In the direct approach, supercritical CO$_2$ is injected and reacted with Ca–Mg–Fe-rich rock containing metal oxide (such as CaO), resulting in the formation of carbonates.
It has the advantage of trapping CO$_2$ at temperatures above 600 °C [12,18]. However, this operation possesses certain shortcomings, such as large amounts of heat and pressure consumption to activate the reactivity of carbonation. To reduce the activation energy, an indirect approach as an aqueous technique is proposed. CO$_2$ absorption in the indirect approach involves transforming the phase of CO$_2$. CO$_2$ through its ionic form (CO$_2^{3-}$ or HCO$_3^-$) spontaneously reacts with metal ions (such as Ca$^{2+}$) then precipitates to form carbonates [17]. Furthermore, cost estimation of CO$_2$ absorption in aqueous alkanolamine consumes USD 62–80 per ton of CO$_2$ [19,20], whereas direct CO$_2$ capture consumes USD 125–335 per ton of CO$_2$ [21].

Integrated absorption–mineralization (IAM) [22] refers to the process of desorbing and mineralizing CO$_2$ captured by aqueous alkanolamine solvents, which has been developed to mitigate the cost of CO$_2$ removal, low carbonate utilization, and environmental concerns in the long term. To minimize the intense energy requirement and improve CO$_2$ capture efficiency, the absorbent absorbs CO$_2$ from the atmosphere and carries it to mineralize through three processes—absorption, precipitation, and regeneration. Moreover, IAM processes were further developed by repeating those processes to maximize the usage of recycled absorbents and improve the formation of carbonates, despite gradual absorbent degradation during IAM cycles [22,23]. Thus, multicycle integrated CO$_2$ absorption–mineralization (multicycle IAM) applies to the reproducible process of absorption, precipitation, and regeneration by reusing the absorbent multiple times [24].

The mineral supplement for mineralizing CO$_2$ absorption comes from industrial brine waste, for instance, byproducts of oil refineries, power plants, textile and leather processing, desalination, and mining. The brine waste is composed of exceedingly intense concentrations of metal ions such as Na$^+$, Ca$^{2+}$, and Mg$^{2+}$ ions, including various contaminants. Instead of treatment, these brine wastes are applied in precipitation to form carbonates [17,24]. The general separation technology and membrane spent USD 0.75–2.5 million and USD 1–1.5 million for 100 gallons per minute, respectively [25,26]. The multicycle IAM can offer high productivity without disrupting or reorganizing the current processes in manufacturing systems.

The conventional absorbent used in the industrial CO$_2$ removal technology is an amine-based solution because of its CO$_2$ capture capacity and ease of modification. Alkanolamine-based absorbents contain two functional groups: (a) the amino group (RNH$_2$, RNH, and RN; R is the alkyl group), which is involved in CO$_2$ capture; and (b) the hydroxyl group (OH), which offers solubility in an aqueous solution. Alkanolamine absorbents can be classified into primary, secondary, tertiary, and steric hindrance amines [27,28].

Monoethanolamine (MEA), a primary amine, is commonly used for gas scrubbing on an industrial scale because it has high CO$_2$ capture performance and reasonable cost [28,29]. Furthermore, aqueous MEA solution was used as in multicycle IAM, and the preliminary results suggested that the regenerated MEA could be efficiently recycled in the gas scrubber without the treatment process and that it increased CO$_2$ absorption and conversion [24]. Even though the MEA absorbent was suitable for CO$_2$ removal, its high energy consumption and erosiveness have raised environmental concerns [30]. In addition, the oxidative and thermal degradation of MEA obstructed its CO$_2$ capture performance [31].

To minimize the disadvantages of MEA, alternative alkanolamine-based absorbents were examined. For instance, diethanolamine (DEA) and triethanolamine (TEA) as secondary and tertiary amines are ethanolamide derivatives obtained from MEA production. In addition, aminomethyl propanol (AMP) as a steric hindrance amine involves the combination of primary and secondary amine structures in the amino group.

Therefore, the absorbent type is a significant factor that can explain why these absorbents suit multicycle IAM. In this study, various aqueous alkanolamine absorbents such as MEA, DEA, TEA, and AMP were used in multicycle IAM, and their ability to transform CO$_2$ gases into insoluble carbonates has been investigated in conjunction with the absorbent properties.
Multicycle IAM starts with the absorption of CO$_2$ emissions through the aqueous alkanolamine absorbent. The primary (RNH$_2$), secondary (RNH), and steric hindrance (RNH$_2^+$) amines are able to form both carbamate and bicarbonate ions. Those amines directly react with CO$_2$ gases in the zwitterion mechanism (RNHCOO$^-$), generating bicarbonate ions (HCO$_3^-$) and protonated amine (RNH$_3^+$), as shown in Equations (1) and (2) [32,33].

$$\text{CO}_2 + \text{RNH}_2 \leftrightarrow \text{RNHCOO}^- + \text{RNH}_3^+$$  \hspace{1cm} (1)

$$\text{CO}_2 + \text{RNHCOO}^- + 2\text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^- + \text{RNH}_3^+$$  \hspace{1cm} (2)

According to a specific structure of steric hindrance amine, the large volume of alkyl groups constrained its structure in spins. The unstable carbamate and hydrolysis are easily transformed into the products, resulting in higher capture performance. On the other hand, CO$_2$ gases dissolve in tertiary amine (NH) and form only a bicarbonate ion and protonated amine because its chemical structure misses the N–H bond, as shown in Equation (3) [33]. Furthermore, the carbamate generation pathway provides a higher heat of formation than bicarbonate generation [34].

$$\text{CO}_2 + \text{RN} + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{RNH}_3^+$$  \hspace{1cm} (3)

Then, in the precipitation process, the bicarbonate ion and protonated amine from the carbamate and bicarbonate formations react with metal ions (Ca$^{2+}$ and Mg$^{2+}$ ions) contained in the solution [35] to produce insoluble carbonates (Equations (4) and (5)) [36,37], as follows:

$$\text{HCO}_3^- + 2\text{RNH}_3^+ + \text{CaCl}_2 \rightarrow 2\text{RNH}_3\text{Cl} + \text{CaCO}_3$$  \hspace{1cm} (4)

$$\text{HCO}_3^- + 2\text{RNH}_3^+ + \text{MgCl}_2 \rightarrow 2\text{RNH}_3\text{Cl} + \text{MgCO}_3$$  \hspace{1cm} (5)

Furthermore, the precipitation process is performed twice to enhance carbonate production. At the end of a cycle, in the regeneration process, the used alkanolamine absorbent is prepared to absorb CO$_2$ emissions in the next cycle by injecting a nonreactive gas (N$_2$) to regenerate the absorbent without internal changes [38]. The regenerated absorbent is repeatedly used through multicycle IAM until it is no longer used.

In this research, the characteristics of absorption and conversion were examined using aqueous alkanolamine-based absorbents such as MEA, DEA, TEA, and AMP through the multicycle integrated CO$_2$ absorption–mineralization (multicycle IAM). Parameters such as CO$_2$ absorption capacity and rate, CO$_2$ conversion, absorbent degradation, and optimal operation time were considered. The production of carbonates can be sufficient in several industries such as construction (building material), textile, plastic, paint, and agriculture [39].

2. Materials and Methods

Four aqueous alkanolamine absorbents were examined during the three steps of multicycle integrated CO$_2$ absorption–mineralization (multicycle IAM)—absorption, precipitation, and regeneration between 20 °C and 25 °C at atmospheric pressure (standard conditions). MEA (>99.0%, Chemical Abstract Service (CAS): 141-43-5), DEA (>99.0%, CAS: 111-42-2), TEA (>99.0%, CAS: 102-71-6), and AMP (>99.0%, CAS: 124-68-5) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and prepared with deionized water at concentrations of 5, 10, and 15 wt.%. CaCl$_2$ (22,000 ppm) and MgCl$_2$ (21,000 ppm) were dissolved in deionized water to prepare a brine solution [17]. In the feed line, 13.0 vol.% CO$_2$ contained CO$_2$ (>99%) and N$_2$ (>99%) to model the flue gas. Furthermore, aqueous alkanolamine solutions were regenerated by pure N$_2$.

The first cycle of IAM is called cycle 1, and the cycles after the regeneration are sequentially called cycles 2 and 3. The experimental equipment used is shown in Figure 1.
2.1. Absorption

On a laboratory scale, the absorber was designed to have a 60 mm inner diameter and 30 cm height. The device precisely controlled 13.0 vol.% CO\textsubscript{2} in 180 mL/min of inlet mixed gas through the flowmeters. The CO\textsubscript{2} concentration of the column outlet was measured with the CO\textsubscript{2} sensor (nondispersive infrared type, range: 0.04–20.0 vol.%, Ichinen Jikco Co., Ltd., COZY-1, Tokyo, Japan) [40]. Pure N\textsubscript{2} (30 mL/min) was injected into the column for 10 min to remove air and humidity before CO\textsubscript{2} absorption. The mixed gas was fed into the column containing a 300-mL aqueous alkanolamine absorbent (Table 1), and the absorbent extended its limit when the CO\textsubscript{2} concentration at the outlet became 13.0 vol.%. The CO\textsubscript{2} absorption capacity of the absorbents was investigated.

The CO\textsubscript{2} absorption capacity [41] is a function of gas flow rate, gas composition, and absorption time, as described in Equation (6):

$$A_c = \frac{PM}{R T m} (y_o - y_i) Q \Delta t$$

(6)

where \(A_c\) is the number of moles of CO\textsubscript{2} absorbed per mole of absorbent, \(P\) is the standard pressure, \(M\) is the molecular weight of CO\textsubscript{2}, \(R\) is the gas constant (8.314 m\textsuperscript{3}.Pa·K\textsuperscript{-1}.mol\textsuperscript{-1}), \(T\) is the standard temperature, \(m\) is the absorbent mass, \(y\) is the gas composition, \(i\) and \(o\) are the inlet and the outlet, respectively, \(Q\) is the gas flow rate at standard conditions, and \(\Delta t\) is the time between the start and end of CO\textsubscript{2} absorption. Furthermore, the CO\textsubscript{2} absorption rate describes the speed of absorption, which is defined as the CO\textsubscript{2} absorption capacity per unit time.

2.2. Precipitation

Precipitation was performed twice to decrease the number of IAM cycles while maintaining the performance of CO\textsubscript{2} absorption and conversion. In the first precipitation, the aqueous alkanolamine absorbent saturated with CO\textsubscript{2} (300 mL) was mixed with a 100-mL brine solution. Solid carbonates spontaneously formed within a few seconds; the mixture reached a steady state when strung for 30 min at 500 rpm. The carbonates were filtered via a filter paper (No.5A, 150 mm) and dried for 10–20 min by heating (60 °C). In the second precipitation, 50 mL of additional brine solution was fed to extract more carbonates using the same process.

Nevertheless, the volume increase (150 mL) with the addition of the brine solution in every precipitation process was abandoned to maintain the initial volume of the absorbent. This is necessary to ensure the accuracy of CO\textsubscript{2} absorption capacity calculations.
2.3. Regeneration

The absorption column was then used as the regenerator to eject CO$_2$ residual gases in the mixture (300 mL) by injecting 30 mL/min of pure N$_2$. The regeneration process was completed when the CO$_2$ concentration at the outlet decreased to below 0.04 vol.%. The regenerated aqueous alkanolamine absorbent was repetitiously used in the next cycle of CO$_2$ absorption.

The cycle of IAM for each alkanolamine absorbent finished when no more carbonates precipitated.

Table 1. Properties of alkanolamine-based absorbents collected data from literature. Vega et al., 2018 [28] identified chemical structure of amines. Chen et al., 2018 [42] summarized limitations of various amines. Smith 1995 [43] created a program of chemical structure of amines. Rinker et al., 1996 [44] explained the advantages and disadvantages of MEA, DEA, and AMP. Liu et al., 2021 [45,46] explained the advantages and disadvantages of TEA.

| Alkanolamine               | Classification      | Chemical Structure | Advantage                                      | Disadvantage                                      |
|----------------------------|---------------------|--------------------|------------------------------------------------|--------------------------------------------------|
| Monoethanolamine (MEA)     | Primary amine       | OH$_2$C$_2$H$_4$–NH$_2$ | • High absorption capacity                      | • Unusable for mixed gases                        |
| Diethanolamine (DEA)       | Secondary amine     | HN(CH$_2$CH$_2$OH)$_2$ | • Using in gas scrubber                        | • High corrosiveness                              |
|                            |                     |                    | • High absorption capacity                      | • High toxicity                                  |
|                            |                     |                    | • Low corrosiveness                             | • High energy consumption                        |
|                            |                     |                    | • Low degradation                               |                                                  |
|                            |                     |                    | • Low toxicity                                  |                                                  |
| Triethanolamine (TEA)      | Tertiary amine      | N(CH$_2$CH$_2$OH)$_3$ | • Stability                                     | • Low absorption capacity                        |
|                            |                     |                    | • Low corrosiveness                             | • High viscosity                                 |
|                            |                     |                    | • Low degradation                               | • High cost                                      |
|                            |                     |                    | • Low toxicity                                  |                                                  |
| Aminomethyl propanol (AMP) | Steric hindrance amine | H$_2$NC(CH$_3$)$_2$CH$_2$OH | • High absorption capacity                      | • High viscosity                                 |
|                            |                     |                    | • Low corrosiveness                             | • High toxicity                                  |
|                            |                     |                    |                                                  | • High cost                                      |

3. Results

In multicycle integrated CO$_2$ absorption–mineralization (multicycle IAM), which includes absorption, precipitation (first and second), and regeneration, the characteristics of MEA, DEA, TEA, and AMP were investigated. In cycle 1, the absorbent exhibits its full performance in terms of CO$_2$ absorption. The next absorptions involve reabsorption by reusing the absorbent, precipitation, and regeneration, named as cycles 2 and 3.

3.1. Effects of the Developed Model of CO$_2$ Absorption Capacity

The formula of the CO$_2$ absorption capacity was altered to be more accurate with the additional functions of temperature, pressure, and gas constant, as mentioned in Equation (6). Due to the reuse of the aqueous MEA absorbent in multicycle IAM, the CO$_2$ absorption capacity was investigated in the first absorption (cycle 1) with 5, 10, and 15 wt.% MEA under standard conditions. The experimental results of MEA were validated with the developed model of CO$_2$ absorption capacity, as shown in Figure 2.

The variation in MEA concentration is related to the CO$_2$ absorption capacity: higher concentrations slightly impact the absorption capacity compared with lower concentrations. The average CO$_2$ absorption capacity was 574.33, 528.86, and 503.95 g of CO$_2$ absorbed per kilogram of MEA solvent when MEA concentration was 5, 10, and 15 wt.%, respectively. The calculation error of CO$_2$ absorption capacity ranged from 2.74 to 16.20%. Furthermore,
these results were similar to those reported in the literature \cite{17,24,46–48}. However, the amount of CO$_2$ absorbed varied because of independent factors, such as human error or external factors. Therefore, the model of CO$_2$ absorption capacity was used for DEA, TEA, and AMP for more accuracy.

![Figure 2. Validated curve of CO$_2$ absorption capacity in aqueous MEA absorbent adapted from literature. Kang et al., 2016 \cite{17} used a stirred reactor with 400 mL of 5, 10, and 30 wt.% of aqueous MEA and 290 mL/min of 15 vol.% of CO$_2$ diluted in flue gas (temperature varied from 25 to 70 °C and atmospheric pressure). Huertas et al., 2015 \cite{41} used a stirred reactor with 500 mL of <50 wt.% solvent and <1 mL/min of 50 vol.% of CO$_2$ gas injection (temperature controlled 25 °C and atmospheric pressure). Yeh and Bai, 1999 \cite{47} used a reactor with 200 mL of 7–35 wt.% solvent and 2–10 mL/min of 8–16 vol.% of CO$_2$ diluted in clean air (temperature varied from 10 to 40 °C and atmospheric pressure), which further calculated absorption capacity in different temperature from Zhu et al., 2011 \cite{48}. The curve was fitted to the Allometric1 model in Origin software (data analysis software) \cite{49}.

3.2. Effects of the Increased Number of Precipitation Steps

The previous study \cite{24} showed a single step of precipitation under standard conditions, whereas we performed precipitation twice (100 and 50 mL), and the results were compared, as shown in Figure 3.

![Figure 3. Difference of carbonate generation between precipitation in single and double steps in multicycle IAM.](image)
In Figure 3, the general bars refer to the previous study (single step of precipitation), and the strip pattern bars refer to the current study (double steps of precipitation). The double steps of precipitation reduced the number of IAM cycles from 11 to 9 while preserving the efficiency of CO\textsubscript{2} absorption capacity. To increase the steps of precipitation, more solid carbonates were generated from the CO\textsubscript{2}–MEA mixture, approximately 23.89–34.08\%. In addition, the overall absorption time was slightly reduced by 4.11\%. Hence, in this experiment, precipitation was repeated twice to improve the yield of carbonate production, including the reduction of the operation time in multicycle IAM.

3.3. Comparison of Absorption in Alkanolamine Absorbents

MEA was extended as a result of the precipitation’s increasing steps. In order to compare these experimental results with those of other absorbents that were extensively investigated in this study, such as DEA, TEA, and AMP, through the repeated cycle of integrated absorption–mineralization (multicycle IAM), two parameters, CO\textsubscript{2} absorption capacity and CO\textsubscript{2} absorption rate, were examined to determine the characteristics of CO\textsubscript{2} absorption in all those aqueous alkanolamine-based absorbents. Experiments were conducted at varying concentrations from 5, 10, and 15 weight percent.

3.3.1. CO\textsubscript{2} Absorption Capacity

The amount of CO\textsubscript{2} absorbed in each alkanolamine absorbent, which evaluates the absorption process in the multicycle integrated absorption–mineralization cycle (multicycle IAM), is described by the CO\textsubscript{2} absorption capacity (Equation (4)) [41]. In multicycle IAM, the first cycle demonstrates the maximum CO\textsubscript{2} absorption capacity of the fresh absorbent. For optimal resource use, the alkanolamine absorbents are prepared for multiple uses. As a result, the purpose of recycled absorbents can enhance CO\textsubscript{2} absorption. Therefore, the amount of CO\textsubscript{2} absorption capacity is defined as the total of each absorbent’s CO\textsubscript{2} absorption capacity during each cycle. Although all aqueous alkanolamine absorbents with the highest concentration (15 wt.\%) had the highest CO\textsubscript{2} absorption capacity, these quantities were not considerably bigger than the lowest concentration (5 wt.\%), as shown in Figure 4a,c. In addition, the rate of CO\textsubscript{2} absorption capacity will discuss how rapidly a 5 wt.\% concentration of those absorbents ran (Section 3.3.2).

Figure 4 shows the CO\textsubscript{2} absorption capacity of 5, 10, and 15 wt.\% aqueous alkanolamine absorbents at equilibrium for each cycle. The amount of absorbed CO\textsubscript{2} was expressed in unit of grams of CO\textsubscript{2} per kilogram of the absorbent. Cycle 1 of the experiment demonstrates the maximum CO\textsubscript{2} absorption capacity for MEA, DEA, TEA, and AMP absorbents, which was 407.42, 113.37, 34.21, and 79.77 g CO\textsubscript{2}/kg absorbent, respectively. As the cycle was repeated (>2 cycles), the amount of CO\textsubscript{2} absorbed in each absorbent dropped to less than 30 g CO\textsubscript{2}/kg absorbent. The contribution to the cumulative effect >2 cycles was therefore small; 5 wt.\% MEA, DEA, and AMP provided higher reabsorption values than the higher concentrations of these absorbents as 73.88, 63.02, and 71.93 g CO\textsubscript{2}/kg absorbent, respectively, whereas 15 wt.\% TEA provided 96.01 g CO\textsubscript{2}/kg absorbent (Figure 4a).

The order of the amount of CO\textsubscript{2} absorption capacity was MEA >> DEA > AMP > TEA, in which MEA had a much higher amount than those of DEA and AMP, while the yield of TEA was the lowest in cycle 1. On the other side, the amount of CO\textsubscript{2} absorption capacity in >2 cycles of MEA, DEA, and AMP was small, whereas the result of TEA was 68\% of the total CO\textsubscript{2} absorption capacity in the completed cycle.

In conclusion, the concentration of the aqueous alkanolamine absorbents MEA, DEA, TEA, and AMP slightly affected how much CO\textsubscript{2} they could absorb. The operating time of finished IAM cycles was improved by the lower absorbent content (5 wt.\%). By using a fresh absorbent at cycle 1, the maximum capacity for each absorbent was obtained. In cycle 1, MEA had the maximum CO\textsubscript{2} absorption capacity (407.42 g CO\textsubscript{2}/kg absorbent). In contrast with >2 cycles, the amount of CO\textsubscript{2} absorption capacity in each absorbent was gathered lower than 30 g CO\textsubscript{2}/kg absorbent. TEA profited from >2 cycles, with the maximum value being 96.01 g CO\textsubscript{2}/kg absorbent.
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Furthermore, Figure 4 compares the amount of CO$_2$ converted with the amount of CO$_2$ absorbed in each absorbent. It is difficult to compare all aqueous alkanolamine absorbents based on CO$_2$ absorption capacity because their utilization depends on the viability of their applications. The amount of carbonate generation will be discussed in the next section (Section 3.4).
3.3.2. CO₂ Absorption Rate

The CO₂ absorption rate, which is expressed in CO₂ absorbed per kilogram of absorbent per unit of time, indicates how much CO₂ is absorbed in an aqueous absorbent during the operating time. In cycle 1 of multicycle IAM, the CO₂ absorption rate profiles demonstrated a similar direction, which gradually reduced, as shown in Figure 5. The concentration of each absorbent was related to the absorption rate due to the amount of absorbed CO₂ divided by a unit of the absorbent. Furthermore, the absorption rate was governed by the absorbent’s viscosity, depending on its concentration [41]. The molecules of CO₂ gases were difficult to spread in high absorbent concentrations, which has a high viscosity, resulting in a low absorption rate.

Figure 5 shows that the highest CO₂ absorption rate of MEA, DEA, TEA, and AMP absorbents was 7.40, 3.51, 3.15, and 4.12 g CO₂/kg absorbent s⁻¹ (Tables S3, S6, S9, and S12), respectively, as impacted by their lowest concentration (5 wt.%). Because MEA has more N–H functions than DEA does in its structure, it can produce more stabilized zwitterion to increase CO₂ absorption [50]. AMP offered a rather high rate since the stand N–H in its planar form favored absorbing CO₂ [33]. Similar tendencies in cycle 1 were seen in the rate profiles of MEA, DEA, and AMP, which drastically initially decreased before becoming moderately reduced. Conversely, the rates of TEA were gradually decreasing.

The operation time in cycle 1 of MEA appeared to be the highest of all concentrations, taking up to 2.27 h at a concentration of 5 wt.%, compared with DEA, TEA, and AMP, which took 47, 4.17, and 16.67 min, respectively.

As noted, these CO₂ absorption results in MEA were slightly different compared with the previous study [24] as a result of the incomplete control of the gas phase. CO₂ gases as a dispersed phase exhibit nonuniform flow in aqueous MEA; therefore, the rate of CO₂ absorption capacity slightly differed due to inconsistent gas–liquid mixing.

Figure 6 represents the rate of CO₂ absorbed in each absorbent in the repeat cycles of IAM (>2 cycles). The concentrations of each absorbent remained to have an influence on the rate of CO₂ absorption capacity over the operation time. However, low concentrations (5 wt.%) had a significant positive effect on these rates in each succeeding cycle. However, in cycle 2, the highest rates of CO₂ absorption for 5 wt.% MEA, DEA, TEA, and AMP absorbents were 1.49, 1.54, 2.10, and 2.19 g CO₂/kg absorbent s⁻¹ (Tables S3, S6, S9, and
S12), respectively. This rate had decreased to an average of 54% compared with cycle 1. Then, the absorbents’ rates declined from 30% to 10%.

(b) The operation time in cycle 1 of MEA appeared to be the highest of all concentrations, whereas the comparison of cycle 1 as fresh absorbents (Figure 5) and >2 cycles as the previous study [24] as a result of the incomplete control of the gas phase. CO₂ absorption for 5 wt.% MEA, DEA, TEA, and AMP was 7.40, 3.51, 3.15, and 4.12 g/kg absorbent sec, respectively, as impacted by their lowest concentration (5 wt.%). Because MEA has more N functions than DEA does in its structure, it can produce more stabilized zwitterion to increase CO₂ absorption [50]. AMP offered a rather high rate since the stand took up to 2.27 g/kg absorbent sec with 0.07% CO₂ at lower viscosities or absorbent concentrations. Thus, the injected CO₂ absorption as 7.40 g/kg absorbent sec in >2 cycles of multicycle IAM. The rate was evaluated by the amount of absorbed CO₂ in every 10 s (Tables S1–S12).

(c) In summary, the CO₂ absorption rates at (a) 5, (b) 10, and (c) 15 wt.% aqueous MEA, DEA, TEA, and AMP in >2 cycles of multicycle IAM. The rate was evaluated by the amount of absorbed CO₂ in every 10 s (Tables S1–S12).
The amount of CO₂ absorbed over time in MEA absorbents was noticeably reduced by 80% due to the comparison of cycle 1 as fresh absorbents (Figure 5) and >2 cycles as recycled absorbents (Figure 6). DEA and AMP had CO₂ absorption rates in >2 cycles that were comparable with MEA, whereas TEA had the opposite results. In addition, the operation time in >2 cycles corresponded to CO₂ absorption rates of each absorbent; that time is reduced for every repeated cycle in a multicycle IAM.

In summary, the CO₂ absorption rates of aqueous alkanolamine absorbents, MEA, DEA, TEA, and AMP were controlled by their concentration. In multicycle IAM, the results of cycle 1 indicated the maximum capacity for each absorbent due to the use of fresh absorbent. As shown in Figure 5, the lower absorbent concentration substantially affected higher concentrations because of the amount of absorbed CO₂ divided by the unit of absorbent and absorbent viscosity. Thus, the injected CO₂ gases were easier to dissolve at lower viscosities or absorbent concentrations. MEA (5 wt.%) provided the highest rate of absorption as 7.40 g·CO₂/kg·absorbent s⁻¹ (Table S3). However, during the first and the next cycles of IAM, the rate of CO₂ absorption in each absorbent decreased by 80, 54, 37, and 45% for MEA, DEA, TEA, and AMP, respectively (Figure 5). These gaps were found to comply with the absorbent degradation. Hence, MEA was intensely degraded up to 80% of the initial CO₂ absorption rate in >2 cycles, whereas the other absorbents were slightly degraded, despite having similar degradation after cycle 2 (30% to 10%).

Since its first operation, MEA has produced positive outcomes in terms of both the capacity and rate of CO₂ absorption. At a concentration of 5 wt.%, MEA required up to 2.81 h of operation time to achieve those values. Therefore, there was extensive discussion regarding the employment of MEA in multicycle IAM.

However, TEA and AMP were two outstanding candidate absorbents for multiple uses. Only 30% to 10% of TEA might be lost during each cycle, and 5 wt.% regenerated TEA could be reused up to 10 times, accumulating more than 68% of the CO₂ absorption capacity during the completed cycle. On the other hand, the regenerated AMP offered the rather high CO₂ absorption capacity and rate throughout the operation, 151.74 g·CO₂/kg·absorbent and 4.12 g·CO₂/kg·absorbent s⁻¹ (Table S12) within 36.33 min.

3.4. Comparison of Conversion in Alkanolamine Absorbents

Solid carbonate is the key achievement of multicycle IAM. In the process of precipitation, the brine solution, containing Ca²⁺ and Mg²⁺ ions, is supplied into the mixture of dissolved CO₂ gases in aqueous alkanolamine absorbents to generate insoluble carbonates. Therefore, two steps of precipitation were added in these experiments to increase carbonate generation. Furthermore, CO₂ conversion was indicated by the amount of mixture converted into the amount of carbonate generation. The conversion of CO₂ absorbed into carbonate is one of the parameters to identify the optimal adsorbent in order to improve the CO₂ utilization by repeating the IAM cycle.

Figure 4 presents the amount of carbonate generation in the unit of grams of carbonate mixture per kilogram of the absorbent in every cycle. The higher amount of carbonate generation in each cycle was caused by the higher concentration of these absorbents based on the greater amount of CO₂ absorption capacity. For the IAM cycle, in cycle 1, the amount of solid carbonate was found to be smaller than the amount of CO₂ absorbed in each absorbent because CO₂ molecules bonded in the function of N–H in the absorbent; thus, the performance of CO₂ capture was declined in cycle 2 due to absorbent degradation. For example, for 5 wt.% concentration, the amount of solid carbonate recovered from MEA, DEA, and TEA decreased by one-third, whereas, for AMP, it decreased by half between cycle 1 and cycle 2. In contrast, the CO₂ absorption capacity sharply reduced, especially for MEA. However, the cumulative amount of solid carbonate raised approximately 3.3–7.5 times for MEA, DEA, and AMP, and up to 12 times for TEA compared with that in cycle 1. As a result, the multicycle IAM has the ability to gather the amount of carbonate production throughout every subsequent cycle.
Despite losses occurring during the transformation of the amount of CO$_2$ absorbed in absorbent to carbonates, as illustrated in Figure 4, the amount of carbonate generation was in the order of MEA >> AMP > DEA > TEA. Compared with cycle 1, the cumulative amount of solid carbonate of TEA was the highest. Interestingly, in the case of MEA, the cumulative amount of solid carbonate in >2 cycles was pretty small. Although MEA had the highest CO$_2$ absorption capacity, its ability to recover solid carbonate was low in the repeated cycles. As a result of the low recovering process of MEA, a large degradation in MEA occurred. Nevertheless, DEA and AMP were similar to MEA in terms of solid carbonate accumulation in >2 cycles.

4. Discussion

IAM processes sought to improve the amount of carbonate generation from CO$_2$ absorbed in the absorbent by reusing the absorbent in many cycles. One of the criteria for selecting the most suitable absorbent to enhance CO$_2$ storage and utilization was the conversion of absorbed CO$_2$ into carbonate. The experiments were performed using aqueous MEA, DEA, TEA, and AMP absorbents under standard conditions through multicycle IAM, which involved the repetition of absorption, precipitation, and regeneration. The solid carbonates were formed by reacting the brine solution with the dissolved CO$_2$ in the absorbent. The reused absorbent could be recycled until its degradation. Moreover, the degradation of the absorbent was examined under various conditions. The effects of concentration, CO$_2$ absorption capacity and rate, carbonate generation, and CO$_2$ conversion were investigated.

4.1. Degradation of Alkanolamine Absorbents

The recycled aqueous alkanolamine absorbent was utilized to extract maximum efficiency due to the operation of the multicycle IAM. However, it is obvious that some of the absorbents’ capability, such as their ability to absorb CO$_2$, was lost throughout cycles 1 and 2 (Figure 4). Degradation of the absorbent is the presence of a decreasing CO$_2$ capture performance [24].

During the operation of the cycle of IAM, unwanted reactions and uncontrollable degradation of the absorbents during the absorption process by autoxidation occurred (oxidative degradation). The ability to capture CO$_2$ was decreased when the products were oxidized to the function of N–H in the absorbent [51]. In addition, heat is released in solid carbonate formation during the precipitation process in which the absorbent molecules were degraded in each cycle (thermal degradation); thus, the efficiency of CO$_2$ absorbed in each absorbent was lower [52,53]. By dividing the difference in CO$_2$ absorption capacity during that cycle by the CO$_2$ absorption capacity in cycle 1, the degradation efficiency of the absorbent was determined by finding out the mechanism of absorbent degradation as follows:

\[
\text{Degradation efficiency} = \frac{A_{c,0} - A_{c,n}}{A_{c,0}} \times 100\%
\]

where $A_{c,0}$ and $A_{c,n}$ are the initial CO$_2$ absorption capacity in cycle 1 and CO$_2$ absorption capacity at cycle $n$, respectively.

The fresh absorbent’s capacity to absorb CO$_2$ was maximum in cycle 1. We assumed that cycle 1 would not undergo significant degradation. On the other side, >2 cycles, the ability of the absorbent to absorb CO$_2$ throughout each cycle was calculated in order to examine the absorbent degradation, as shown in Figure 7.

Figure 7 displays the degradation efficiency of each absorbent through the cycle of IAM. If an absorbent’s degradation efficiency approaches 100%, it indicates that the absorbent has lost its capacity to absorb CO$_2$. As a consequence, an absorbent that can be utilized in the IAM cycle multiple times should have a low degradation efficiency since the initial cycle.
The concentration of the absorbent was found to comply with absorbent degradation. For each concentration, the degradation efficiency extremely increased in cycle 2 and slightly next cycle in order. High concentration (15 wt.%) had a vast effect on the degradation efficiency (more than 85%) than the lower concentrations, disrupted by the uncontrollable side reactions, resulting in the reducing ability of CO$_2$ capture. Hence, the lowest concentration, 5 wt.%, might avoid the higher degree of degradation in each absorbent.

In cycle 2, the degradation efficiency of 5 wt.% MEA started at 92.22%, resulting in lower performance of CO$_2$ capture in repeated cycles. An amount of 5 wt.% DEA and AMP showed a moderate value in which the absorbent degraded by 77.48% and 64.02%. Although Equations 1 and 2 show that MEA, DEA, and AMP can produce carbamate and bicarbonate ions, the rates of CO$_2$ absorption capacity are different [32,33]. It is contrary to TEA, which barely degraded (43%) because of its symmetric structure [33]. Although TEA has the potential to enhance both reuse and degradation efficiency, the CO$_2$ absorption capacity and carbonate generation still need considerable improvement. As a result, AMP is a desirable alternative absorbent for both CO$_2$ absorption capacity and carbonate generation, in which the efficiency of degradation is acceptable.

4.2. CO$_2$ Conversion of Alkanolamine Absorbents

The measurable quantity of absorbed CO$_2$ that can be converted to carbonates is referred to as CO$_2$ conversion. The goal of this study was to improve the production of carbonates by precipitating CO$_2$ that was absorbed in absorbents. As a result, based on CO$_2$ conversion, the absorbent type and concentration, and optimal repeated cycles were determined for maximizing yield in the shortest operation time in the multicycle IAM.

When CO$_2$ is converted, it transforms into new chemical forms that still contain carbon in it. The conversion in this experiment indicates how much of the absorbed CO$_2$ in those absorbents converts to solid carbonates, which is calculated according to Equation (8) [17,54]. The management of carbon included the conversion and use of CO$_2$.

\[
\text{Percent conversion} = \frac{\text{Amount of carbonate generation}}{\text{Amount of CO}_2\text{ absorbed}} \quad (8)
\]

As the IAM cycle is expanded, Figure 8 demonstrates the progression of CO$_2$ conversion of alkanolamine absorbents as a percentage of carbonate generation in relation to the amount of CO$_2$ absorbed. The percentage of CO$_2$ conversion for each concentration of absorbents tends to rise with each following IAM cycle, resulting in more of solid carbonate.
formation produced per unit of CO\textsubscript{2} absorbed. However, the effect of CO\textsubscript{2} conversion was less apparent in some absorbents including MEA, DEA, and AMP in later cycles of operation because the amount of carbonate generation formed throughout that cycle was smaller than the whole amount of CO\textsubscript{2} absorbed. Therefore, the optimal IAM cycle for each absorbent may be determined to produce the most solid carbonate based on the percent CO\textsubscript{2} conversion.

![Figure 8. Percentage conversion of 5, 10, and 15 wt.% MEA, DEA, TEA, and AMP absorbents in multicycle IAM.](image)

In comparison with higher concentrations, 5 wt.% of each absorbent resulted in the best results. DEA and AMP were exceptional absorbents with high percent CO\textsubscript{2} conversion of 72.90% and 86.93%, yet MEA and TEA exhibited percent CO\textsubscript{2} conversion of 59.42% and 54.11%, respectively, in the completed IAM cycle. Additionally, we discovered that four cycles that produced the largest quantity of CO\textsubscript{2} absorbed in AMP were converted into solid carbonate at a percentage of 89.54% when considering the optimal IAM cycle.

As shown in Figure 9, there is a correlation between the amount of CO\textsubscript{2} absorption capacity and CO\textsubscript{2} conversion in each concentration of alkanolamine absorbents at the end of the cycle. This means that when choosing suitable absorbents for a multicycle IAM, it is important to consider these two factors into account.

Two types of absorbents are shown on the graph that have the potential to be employed in multicycle IAM: MEA, which displays the greatest CO\textsubscript{2} absorption capacity; and AMP, which enhances the transformation of absorbed CO\textsubscript{2} into solid carbonate. The use of the AMP absorbent is one way of operating a multicycle IAM to improve CO\textsubscript{2} utilization since more of the absorbed CO\textsubscript{2} could be converted into products, achieving the objective of this research. Compared with MEA, which provides good results in terms of the most CO\textsubscript{2} absorption capacity but consumes the longest time, AMP offers both a relatively high CO\textsubscript{2} absorption capacity and the highest CO\textsubscript{2} conversion in a short operation time. In addition, the degradation efficiency of AMP is acceptable.

For this study, the maximized reused absorbents while enhancing more carbonates were an essential factor; therefore, the most suitable alkanolamine absorbent was selected to fulfill the aim of multicycle IAM. Considering 4 IAM cycles (optimal cycles), we found that 5 wt.% AMP had the highest percent CO\textsubscript{2} conversion compared with the other absorbents. About 89.54% of the amount of CO\textsubscript{2} absorbed was transformed into solid carbonate. Although AMP had moderate CO\textsubscript{2} absorption capacity and rate, their potential for CO\textsubscript{2} conversion was promising for long-term CO\textsubscript{2} removal, capture, and sequestration. In the completed multicycle IAM for 5 wt.%, AMP (33 min) were five times faster than MEA...
Therefore, AMP might offer both high CO₂ capture performance and carbonate generation within a short operation time.

Figure 9. Correlation between amount of CO₂ absorption capacity and CO₂ conversion in 5, 10, and 15 wt.% MEA, DEA, TEA, and AMP absorbents at the completion of the cycle of multicycle IAM.

5. Conclusions

Various aqueous alkanolamine-based absorbents with differential chemical structures such as MEA, DEA, TEA, and AMP were studied for the optimal operation of multicycle integrated CO₂ absorption–mineralization (multicycle IAM). This research aimed to eliminate large-volume CO₂ emissions that lead to environmental concerns in terms of energy consumption, re-released pollutant, and water disposal. Furthermore, multicycle IAM was developed to improve the efficiency of CO₂ absorption and CO₂ conversion within a shortened operating time. Especially, the degradation of absorbents was evaluated.

The reusable aqueous alkanolamine absorbent, which is durable and active for CO₂ absorption, is a key to the successful operation of the IAM cycle. The study aimed to increase the amount of CO₂ absorbed and converted with reasonable operating costs and environmental concerns. MEA, DEA, TEA, and AMP were used, and the suitable absorbent type was determined based on three parameters—CO₂ absorption capacity and rate, CO₂ conversion, and absorbent degradation over the overall operation time, which is the summation of the total time spent in each cycle.

The experimental results indicated that CO₂ absorption capacity and rate were in the order of MEA >> DEA > AMP > TEA in cycle 1 of IAM. The degradation efficiency of each absorbent was 92.22%, 77.48%, 43%, and 64.02% in MEA, DEA, TEA, and AMP, respectively. On the other hand, >2 cycles of IAM were the most significant parameter for multiple operations in which the rate and capacity of CO₂ were in the order of TEA > AMP ≈ DEA > MEA with similar degradation as 30% to 10% (Figures 5 and 6). The TEA absorbent had excellent repeatability with low degrading efficiency, but CO₂ absorption capacity and rate, carbonate formation, and CO₂ conversion need to be modified. TEA may, therefore, be able to provide an answer in some industries.

In consequence, four-cycle 5 wt.% AMP was the most suitable potential absorbent for the multicycle IAM, providing 143.34 g of CO₂ per kilogram of the absorbent and 128.34 g of carbonates per kilogram of the absorbent (33 min). About 89.5% of the amount of CO₂ absorbed in AMP was converted into carbonates, exceeding previously reported results (5 wt.% MEA, 60% approximately). We expect that the large-scale production of carbonates can be a new source for the construction and agriculture industries. Furthermore, the pH level for disposal water was between 7.2 and 7.8, which was in the range of safe discharge. In addition, the overall operation time of AMP was faster (approximately 5 times) than MEA (2 h), which had the highest CO₂ absorption capacity [24]. It means that the energy
consumption of the AMP was significantly lower than MEA. In addition, 64.02% of AMP was moderately degraded during cycles 1 and 2, and its efficiency in the next cycle (>2 cycles) was orderly decreased to 30%–10%. Therefore, 5 wt.% AMP was the most suitable absorbent for multicycle IAM.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12111386/s1, Table S1. CO$_2$ absorption rate of 15 wt.% MEA over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S2. CO$_2$ absorption rate of 10 wt.% MEA over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S3. CO$_2$ absorption rate of 5 wt.% MEA over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S4. CO$_2$ absorption rate of 15 wt.% DEA over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S5. CO$_2$ absorption rate of 10 wt.% DEA over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S6. CO$_2$ absorption rate of 5 wt.% DEA over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S7. CO$_2$ absorption rate of 15 wt.% TEA over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S8. CO$_2$ absorption rate of 10 wt.% TEA over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S9. CO$_2$ absorption rate of 5 wt.% TEA over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S10. CO$_2$ absorption rate of 15 wt.% AMP over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S11. CO$_2$ absorption rate of 10 wt.% AMP over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$]. Table S12. CO$_2$ absorption rate of 5 wt.% AMP over operation time. [Unit of CO$_2$ absorption rate: g CO$_2$/kg Absorbent s$^{-1}$].

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