

## Article

# Development of CO<sub>2</sub> Absorption Using Blended Alkanolamine Absorbents for Multicycle Integrated Absorption–Mineralization

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**Abstract:** The present study aimed to investigate the feasibility of blended amine absorbents in improving the CO<sub>2</sub> alkanolamine-based absorption of multicycle integrated absorption–mineralization (multicycle IAM) under standard operating conditions (20–25 °C and 1 atm). Multicycle IAM is a promising approach that transforms CO<sub>2</sub> emissions into valuable products such as carbonates using amine solvents and waste brine. Previously, the use of monoethanolamine (MEA) as an absorbent had limitations in terms of CO<sub>2</sub> conversion and absorbent degradation, which led to the exploration of blended alkanolamine absorbents, such as diethanolamine, triethanolamine, and aminomethyl propanol (AMP) combined with MEA. The blended absorbent was evaluated in terms of the absorption performance and carbonate production in continuous cycles of absorption, precipitation/regeneration, and preparation. The results showed that the fourth cycle of the blend of 15 wt.% AMP and 5 wt.% MEA achieved high CO<sub>2</sub> absorption and conversion efficiency, with approximately 87% of the absorbed CO<sub>2</sub> being converted into precipitated carbonates in 43 min and a slight degradation efficiency of approximately 45%. This blended absorbent can improve the efficiency of capturing and converting CO<sub>2</sub> when compared to the use of a single MEA, which is one of the alternative options for the development of CO<sub>2</sub> capture and utilization in the future.



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**Keywords:** absorbent degradation; blended alkanolamine absorbent; carbonate; carbon capture, utilization, and storage; CO<sub>2</sub> absorption capacity; conversion efficiency; degradation efficiency; integrated absorption–mineralization; multicycle

## 1. Introduction

The current global consumption of energy is predominantly reliant on fossil fuels, constituting more than 80% of the total consumption of energy worldwide, as reported by the International Energy Agency [1–3]. The escalation in the production of coal and natural gas over the past two decades has exceeded the global energy demand, leading to a 45% upsurge in CO<sub>2</sub> emissions, which serve as the primary driver of global warming and the ongoing climate crisis [4–8]. In order to achieve carbon neutrality and reduce the carbon footprint, governments worldwide have collaborated in reaching an intergovernmental agreement [9–11]. To maintain the stability of CO<sub>2</sub> levels in the atmosphere, various carbon removal technologies have been developed [12,13].

To address this pressing issue, a concerted global effort is needed in order to reduce carbon emissions and attain carbon neutrality [13]. One promising strategy is carbon capture, utilization, and storage (CCUS) [13–15]. The CCUS technology enables the separation of CO<sub>2</sub> from pollution sources, followed by its utilization or storage, through nonconversion or conversion methods [15]. Over 230 metric tons of CO<sub>2</sub> are captured every year for commercial use, such as enhanced oil recovery. Moreover, alternative approaches are being developed to convert CO<sub>2</sub> into fuels, chemicals, and building materials [15–18]. The production of CO<sub>2</sub>-based building materials allows for the permanent storage of CO<sub>2</sub> in the

form of insoluble carbonates with less energy consumption [19]. The efficiency of CCUS technology depends on numerous factors, including high CO<sub>2</sub> capture performance, low-energy consumption, no risk of CO<sub>2</sub> leakage or explosion, and a minimal environmental impact [19–21].

Multicycle integrated absorption–mineralization (multicycle IAM) provides a promising alternative for mitigating CO<sub>2</sub> emissions through the multiple utilization of aqueous alkanolamine-based solvents. The process allows for the capture and conversion of atmospheric CO<sub>2</sub> into carbonates with low-energy demands through recurring absorption, precipitation/regeneration, and preparation [22–24]. Alkanolamine-based absorption is widely used for capturing CO<sub>2</sub> emissions from current industries. This process involves passing the gas stream through a liquid solvent, which selectively absorbs the CO<sub>2</sub> [25,26]. The conventional absorbent used in industrial CO<sub>2</sub> removal technology is typically an amine-based solution, as it offers a high CO<sub>2</sub> capture capacity and ease of modification [22]. The alkanolamine absorbents contain two functional groups, an amino group (RNH<sub>2</sub>, RNH, and RN; R is the alkyl group) involved in CO<sub>2</sub> capture and a hydroxyl group (OH) offering solubility in an aqueous solution. The absorbent acts as a CO<sub>2</sub> collector during absorption, converting it into an ionic form, such as carbonate or bicarbonate ions [19,22–26]. Primary amines, such as monoethanolamine (MEA), are the most commonly used for CO<sub>2</sub> removal due to their high efficiency. However, secondary, tertiary, and steric hindrance amines are also utilized and offer different advantages such as lower volatility and improved resistance to corrosion [27,28]. In the precipitation/regeneration process, the aqueous carbonation method transforms the dissolved CO<sub>2</sub> into the absorbent when reacted with metal cations, such as calcium and magnesium cations [19–22,29]. These metal cations are collected from brine waste streams generated by oil refineries, power plants, textile and leather processing units, mining industries, and desalination systems [30]. These brine streams, rather than being treated as waste, are utilized to precipitate carbonates, contributing to a more sustainable approach [31]. The high-purity carbonate produced by multicycle IAM provides a competitive alternative to conventionally produced carbonates, opening avenues for market substitution [15–18]. The integration of CO<sub>2</sub> alkanolamine-based absorbent recycling and brine mineralization within the multicycle IAM offers a promising avenue for CCUS technologies. The multicycle IAM has been found to facilitate an increase in carbonate production at ambient temperature and pressure conditions, while maximizing the efficacy of the amine absorbent. These findings present a valuable contribution towards the development of effective climate crisis mitigation strategies, addressing the pressing need for CO<sub>2</sub> emission reduction. Additionally, further research is warranted to fully understand the underlying mechanisms of carbonate production and to optimize the multicycle IAM. This will enable this approach to be more widely applied in industrial-scale CCUS projects, providing a critical pathway towards achieving global carbon neutrality goals [19,22,23].

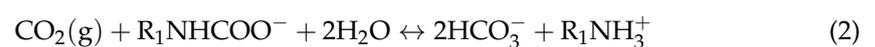
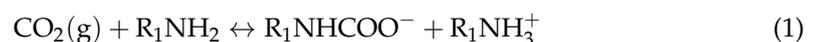
The first-generation absorbent used in multicycle IAM was MEA absorbents, owing to their high CO<sub>2</sub> reactivity and cost effectiveness [22,23]. However, the tendency of MEA for high degradation and energy consumption and its erosiveness raised concerns about its environmental impact and role in reducing CO<sub>2</sub> capture performance [32]. Towards this end, researchers have widely adopted a blending approach to improve the CO<sub>2</sub> absorption and conversion of MEA solvent in multicycle IAM. As such, a blended alkanolamine absorbent offers several advantages in comparison to a single MEA absorbent, including improved CO<sub>2</sub> selectivity; decreased degradation, corrosion, and energy requirement; and cost effectiveness [33–35].

As an alternative to MEA absorbents, secondary and tertiary amines, such as diethanolamine (DEA) and triethanolamine (TEA), and a steric hindrance amine, such as aminomethyl propanol (AMP), have been assessed as potential blending components with MEA [36]. Blended aqueous alkanolamines are an innovative type of absorbent derived from the combination of two amine components, providing a potential alternative for enhancing amine-based absorption and gradually replacing the use of a single alkanolamine solvent [33,37]. Blended alkanolamine absorbents exhibit several advantages over single

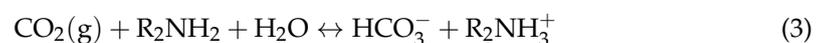
alkanolamine absorbents for CO<sub>2</sub> capture [33–37]. Firstly, the blended alkanolamines can be designed to have a greater CO<sub>2</sub> absorption capacity by leveraging the unique strengths of the different amine structures [38]. Secondly, they can lower the energy requirements for CO<sub>2</sub> capture, as they can be formulated with a lower heat of absorption, necessitating less energy to regenerate the absorbent [33,37]. Furthermore, the blended alkanolamines are often more stable than single alkanolamines owing to their stability and resistance to degradation over time [39–41]. Additionally, an alkanolamine blend can be manufactured from more readily available and lower-cost raw materials, rendering them a cost-effective option for CO<sub>2</sub> capture from large-scale industrial processes. Therefore, blended alkanolamine absorbents offer substantial benefits in terms of the CO<sub>2</sub> absorption capacity and energy requirements, making them a highly promising option for reducing CO<sub>2</sub> [33–37]. In a two amine component system, one component serves to improve the CO<sub>2</sub> absorption capacity (referred to as an activator) and the other to increase the CO<sub>2</sub> absorption rate (referred to as a promoter) [36]. The properties of alkanolamine blends, prepared from primary, secondary, tertiary, and steric hindrance amines, are nonlinear and depend on the amine blending components and concentrations [37]. Therefore, the absorption behavior of these blended absorbents can be described by the individual kinetics of CO<sub>2</sub> absorption [39–41].

Herein, we used an alkanolamine blend containing DEA, TEA, and AMP components in MEA absorbents in multicycle IAM to enhance the CO<sub>2</sub> absorption capacity and rate, conversion efficiency, absorbent degradation, and operation time. The blended alkanolamine absorbents were evaluated in comparison to the single MEA as a reference absorbent under multicycle IAM conditions, considering the different blending components and concentrations [23].

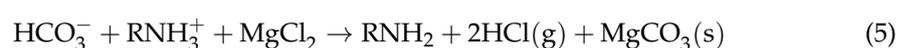
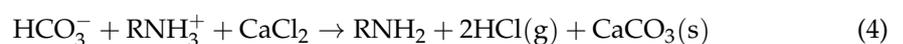
The aqueous alkanolamine blend utilized in multicycle IAM involves three distinct stages: absorption, precipitation/regeneration, and preparation. During the absorption process, CO<sub>2</sub> gases dissolve directly into the blended absorbent composed of primary amines such as MEA, secondary amines such as DEA, and steric hindrance amines such as AMP to form carbamate intermediates. This reaction pathway involving two steps is known as the zwitterion mechanism [37,42], which results in the generation of bicarbonate ions and protonated amine, as demonstrated by Equations (1) and (2).



The dissolution of CO<sub>2</sub> gas in blended absorbents composed of tertiary amines such as TEA and certain steric hindrance amines such as AMP results in the formation of bicarbonate ions and protonated amines [38], as illustrated in Equation (3).



The mechanism of CO<sub>2</sub> absorption in blended alkanolamine absorbents is similar to that of tertiary and steric hindrance amines, as the reaction between CO<sub>2</sub> and the amine group leads to the formation of bicarbonate ions and protonated amines. However, the exact absorption mechanism may vary, given its dependance on various factors, such as the properties of individual amine components and their concentrations in the blend. Thus, despite extensive research, the exact mechanism remains under discussion [36,38]. During the precipitation/regeneration process, the bicarbonate ion and protonated amine from the carbamate and bicarbonate formations react with metal cations in the waste brine solution [43] to produce insoluble carbonates [44,45], as shown in Equations (4) and (5).



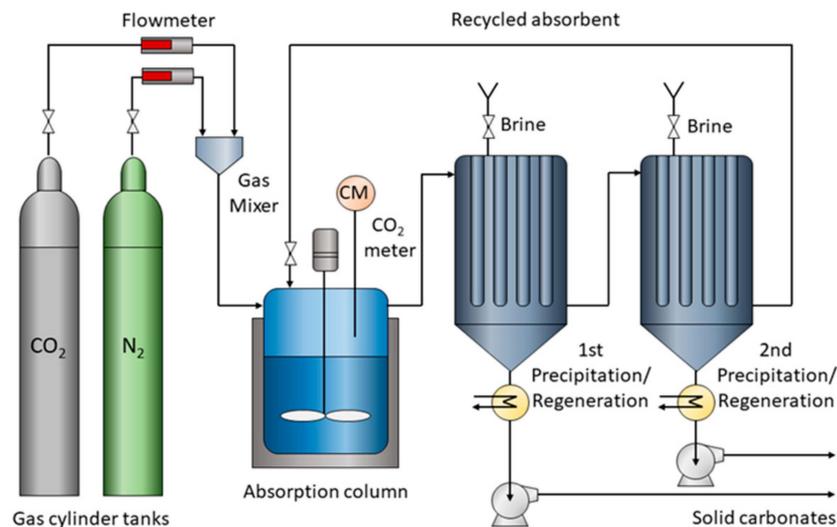
Moreover, performing the double precipitation/regeneration process significantly improves the production of precipitated carbonate. In addition, the blended absorbent automatically regenerates in the precipitation/regeneration process.

In the preparation process, nitrogen gas, a nonreactive gas, is utilized to flush the regenerated blend of alkanolamine, removing the byproduct of acid gas before the absorbent is ready for another CO<sub>2</sub> absorption cycle [46]. The regenerated absorbent is repeatedly employed until no precipitated carbonate is further generated.

Herein, we aimed to enhance the CO<sub>2</sub> absorption performance in multicycle IAM by utilizing aqueous alkanolamine blends at near room temperature (20–25 °C) and atmospheric pressure (1 atm). The blend absorbents consisted of DEA, TEA, AMP, and MEA components. The absorption and conversion potential of the blended alkanolamine absorbents was evaluated based on parameters such as the CO<sub>2</sub> absorption capacity and rate, conversion efficiency, absorbent degradation, and optimal operation time. Furthermore, the performance of the blended absorbents was compared to that of a single MEA absorbent, which was used as a reference [23]. The behavior of the absorbent during multicycle IAM was investigated. To optimize CO<sub>2</sub> absorption and utilization in multicycle IAM, the application of blended alkanolamine solvents can be improved by adjusting the blending components and concentrations to achieve the optimal conversion efficiency and reduced absorbent degradation.

## 2. Materials and Methods

A blend of alkanolamine solvents with varying components, namely, MEA (CAS: 141-43-5; purity: >99.0%), DEA (CAS: 111-42-2; purity: >99.0%), TEA (CAS: 102-71-6; purity: >99.0%), and AMP (CAS: 124-68-5; purity: >99.0%), at concentrations of 5, 10, and 15 wt.% was evaluated to determine their ability to absorb CO<sub>2</sub> in the multicycle IAM process. The blending components were supplied by Kanto Chemical Co., Inc. (Tokyo, Japan), and the absorbent concentrations were prepared using deionized water. The waste brine was prepared with dissolved CaCl<sub>2</sub> (22,000 ppm) and MgCl<sub>2</sub> (21,000 ppm) in deionized water [19]. Moreover, 13.0 vol.% CO<sub>2</sub> in the feed line contained CO<sub>2</sub> (>99%) and N<sub>2</sub> (>99%) to simulate the flue gas. The first cycle of the IAM is called cycle 1, with sequential cycles being cycles 2 and 3. The experimental equipment and devices were set up as shown in Figure 1.



**Figure 1.** Experimental equipment and devices used for the multicycle integrated absorption–mineralization (IAM).

### 2.1. Absorption

The CO<sub>2</sub> absorption performance was evaluated in an absorption column, with an inner diameter of 60 mm and a height of 30 cm, using blended alkanolamine absorbents.

Moreover, 180 mL/min of the inlet mixed gas precisely controlled the CO<sub>2</sub> concentration at 13.0 vol.% through the use of mass flow meters. The CO<sub>2</sub> concentration of the column outlet was measured using a CO<sub>2</sub> meter (nondispersive infrared type, range: 0.04–20.0 vol.%; Ichinen Jikco Co., Ltd., COZY-1, Osaka, Japan) [47]. The absorption column was sterilized to remove the air and humidity, and 30 mL/min of pure N<sub>2</sub> was injected before the next CO<sub>2</sub> absorption [46]. Furthermore, a 300 mL column with blended absorbents was filled with the mixed gas, and this process was repeated until the absorbent reached its limit or when the outlet concentration of CO<sub>2</sub> reached 13.0 vol.%. The CO<sub>2</sub> absorption capacity and rate and degradation efficiency of each absorbent were investigated.

## 2.2. Precipitation/Regeneration

To improve the number of IAM cycles while maintaining the performance of the CO<sub>2</sub> absorption and conversion, precipitation/regeneration was conducted twice. In the initial precipitation, 100 mL brine solution was added to blended absorbents (300 mL), producing the solid carbonate to spontaneously precipitate within a short operation time. Further, a filter paper (No. 5A, 150 mm) was used to filter the solid carbonate, which was then dried for 10–20 min by heating at 60 °C. The solid carbonate was completely mixed after 30 min of stirring at 500 rpm. In the subsequent precipitation, 50 mL of brine solution was added to continue the recovery of carbonates. The amount of carbonate generated was measured. Moreover, the absorbent automatically regenerated simultaneously. To ensure the calculation accuracy of the CO<sub>2</sub> absorbing capacity, the volume of blended absorbent increased by 150 mL in every precipitation was adjusted to maintain the initial volume [23]. The conversion efficiency of each absorbent was examined.

## 2.3. Preparation

For the preparation, 30 mL/min of pure N<sub>2</sub> was injected into the absorption column to emit the acid gas (HCl) [23]. The absorbent was then thoroughly cleaned and prepared for the subsequent cycle of IAM. The multicycle IAM for each blended absorbent was completed when no more solid carbonate was formed during the precipitation/regeneration [22,23].

## 2.4. Parameter

### 2.4.1. CO<sub>2</sub> Absorption Capacity

The measure of an absorbent's ability to absorb CO<sub>2</sub> is referred to as its performance. An increasing absorbent capacity can lead to improved CO<sub>2</sub> utilization by enabling greater CO<sub>2</sub> accumulation for mineralization. The CO<sub>2</sub> absorption capacity is influenced by several factors, including the gas flow rate, gas composition, absorption time, and the applied gas constant. Equation (6) presents a model that describes the CO<sub>2</sub> capture characteristics of blended absorbent solutions [48].

$$A_c = \frac{PM}{RTm} (y_o - y_i) Q \Delta t \quad (6)$$

The CO<sub>2</sub> absorption capacity ( $A_c$ ) in unit of grams of CO<sub>2</sub> absorbed per kilogram of absorbent was calculated using the following parameters: standard pressure ( $P$ ), molecular weight of CO<sub>2</sub> ( $M$ ), gas constant ( $R = 8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$ ), standard temperature ( $T$ ), mass of absorbent ( $m$ ), gas composition ( $y$ ), inlet ( $i$ ) and outlet ( $o$ ), gas flow rate at standard conditions ( $Q$ ), and the difference in time between the start and end of CO<sub>2</sub> absorption ( $\Delta t$ ). The measurement error was estimated to be in the range of 2.74%–16.2% [23,48–50].

Furthermore, the efficiency of CO<sub>2</sub> absorption per unit of time, represented as the accumulation of CO<sub>2</sub> over the operation time, was used to evaluate the rate of absorption. The operation time, which is the sum of the CO<sub>2</sub> absorption time in the multicycle IAM, is defined as the duration required by an absorbent to absorb CO<sub>2</sub>. Notably, reducing the operation time also decreases the capital costs [15–19].

### 2.4.2. Degradation Efficiency

The degradation of alkanolamine absorbent refers to the chemical and physical changes in the amine absorbent solution over time, significantly reducing its ability to effectively absorb and retain CO<sub>2</sub>. In the multicycle IAM, the unnecessary oxidative and chemical reactions generally occur when the alkanolamine absorbent interacts and absorbs CO<sub>2</sub> in the flue gas. These reactions result in the loss of alkanolamine molecules in the absorbent solution through conversion to other substances, such as formaldehyde, acetic acid, vinyl alcohol, and acetaldehyde [51–54].

The amine degradation in the absorbent solution is indicated by the reduction in amine content and the corresponding decline in the CO<sub>2</sub> absorption capacity ( $A_c$ ) [22,23], which is called degradation efficiency. It can be quantified as the difference between the initial absorption capacity and that at any subsequent cycle and can be expressed using Equation (7).

$$\text{Degradation efficiency} = \frac{A_{c,i} - A_{c,n}}{A_{c,i}} \times 100\% \quad (7)$$

where  $i$  represents the initial value, and  $n$  represents the number of cycles.

The degradation of the alkanolamine absorbent used in the multicycle IAM is crucial in determining the potential reuse duration of the absorbent. The degradation efficiency is therefore an essential parameter that must be considered in the optimization of the operational conditions for the multicycle IAM. The assessment of the degradation efficiency can reflect the stability of the absorbent through several cycles and its capacity to perform effectively during the CO<sub>2</sub> absorption process.

The selection criterion for the appropriate alkanolamine absorbent in multicycle IAM was defined as a degradation efficiency lower than 60%, based on the mean degradation efficiency of single absorbent solutions of MEA, DEA, TEA, and AMP at concentrations of 5, 10, and 15 wt.%, which were operated under the same conditions in the multicycle IAM [23].

### 2.4.3. Conversion Efficiency

The performance of multicycle IAM can be effectively evaluated by examining the CO<sub>2</sub> conversion, which represents the amount of absorbed CO<sub>2</sub> that can be converted into precipitated carbonates (Table 1). The CO<sub>2</sub> conversion from the alkanolamine absorbents is calculated as the conversion efficiency [51] using Equation (8).

$$\text{Conversion efficiency} = \frac{\text{Amount of dried carbonate}}{\text{Amount of CO}_2 \text{ absorbed}} \times 100\% \quad (8)$$

**Table 1.** Conventional precipitated calcium carbonate.

|                       | Puthiya Veetil et al., (2021) [55] | Kakizawa et al., (2001) [56]          | Kakizawa et al., (2001) [56]          | Gerdemann et al., (2004) [57] | Teir et al., (2005) [58]              |
|-----------------------|------------------------------------|---------------------------------------|---------------------------------------|-------------------------------|---------------------------------------|
| Conditions            | 23 °C and 1 atm                    | 25 °C and 1 atm                       | 25 °C and 74 atm                      | 185 °C and 150 atm            | 60–80 °C and 1 atm                    |
| Method                | indirect aqueous carbonation       | indirect carbonation with acetic acid | indirect carbonation with acetic acid | direct aqueous carbonation    | indirect carbonation with acetic acid |
| Conversion efficiency | 60%                                | 40%                                   | 75%                                   | >70%                          | 95.6%–98.8%                           |

The conversion of CO<sub>2</sub> into stable chemical forms during the precipitation/regeneration process that retains CO<sub>2</sub> rerelease in the form of valuable products is an essential aspect of CO<sub>2</sub> application and environmental preservation. To optimize the multicycle IAM operation, the conversion efficiency is prioritized, because the present study aimed to increase the CO<sub>2</sub> conversion efficiency at the minimum operational time such that compared to conventional carbonate synthesis, this process can be competitively priced [15–19].

The selection criterion for the appropriate alkanolamine absorbent in multicycle IAM was established as a conversion efficiency higher than 70% [55–58], which was based on the average CO<sub>2</sub> conversion reported in previous studies on conventional precipitated calcium carbonate.

### 3. Results

#### 3.1. Characteristics of CO<sub>2</sub> Absorption

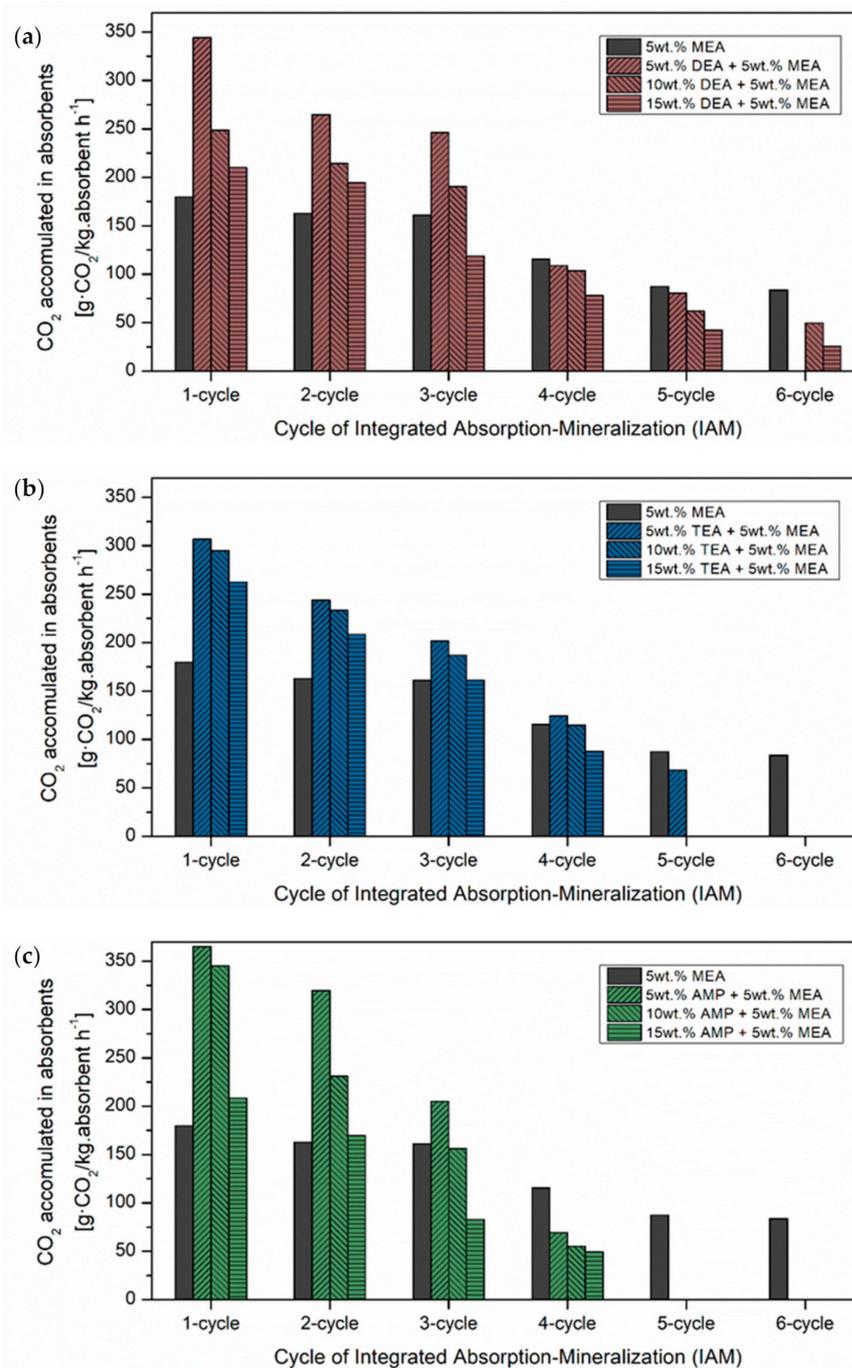
The multicycle IAM operation utilized blended alkanolamine absorbents composed of MEA with components of DEA, TEA, and AMP. These blended absorbents were designed to extend the limitations of CO<sub>2</sub> absorption using single MEA absorbents. The blend concentrations consisted of a constant 5 wt.% of MEA and varying concentrations of DEA, TEA, and AMP at 5, 10, and 15 wt.%. The performance of the blended absorbents was evaluated based on their CO<sub>2</sub> absorption capacity as determined by Equation (6). The CO<sub>2</sub> accumulation of the blended alkanolamine absorbents was quantified as the amount of CO<sub>2</sub> absorbed over time during absorption.

In the multicycle IAM, cycle 1 was characterized by the highest CO<sub>2</sub> absorption capacity of the blended absorbents owing to their freshness. The subsequent cycles also showed improved CO<sub>2</sub> absorption capacities. A comparison of the CO<sub>2</sub> absorption capacity of the blended absorbents with that of the reference single 5 wt.% MEA absorbent was performed to assess the enhancement in performance during the multicycle IAM [33–35,37], as illustrated in Figure 2.

Figure 2 illustrates the CO<sub>2</sub> accumulation in the blended alkanolamine absorbents composed of 5 wt.% MEA and varying concentrations of DEA, TEA, and AMP (5, 10, and 15 wt.%) at equilibrium during each cycle of the multicycle IAM. The accumulated CO<sub>2</sub> is represented as the grams of absorbed CO<sub>2</sub> per kilogram of blended absorbent per unit time. The reference of a single 5 wt.% MEA absorbent is depicted by the gray columns [23]. Compared to the single 5 wt.% MEA absorbent, the blended absorbents demonstrated an improved CO<sub>2</sub> absorption capacity during cycles 1, 2, and 3. However, the CO<sub>2</sub> accumulation decreased for cycle 4 and beyond. Despite this, the number of cycles was reduced in comparison.

When DEA, TEA, and AMP were added, the effectiveness of the blended alkanolamine absorbent in absorbing and accumulating CO<sub>2</sub> was found to be superior to that of the reference 5 wt.% MEA. The addition of these blending components substantially improved the CO<sub>2</sub> absorption performance during the multicycle IAM. The results show that the CO<sub>2</sub> absorption capacity of the blended absorbent over time was substantially higher than that of the single MEA absorbent in cycle 1. The maximum CO<sub>2</sub> absorption capacity of 5 wt.% MEA was 179.74 g·CO<sub>2</sub>/kg.absorbent h<sup>-1</sup> [23]. In contrast, the blended alkanolamine absorbents with a low concentration (5 wt.%) exhibited higher maximum CO<sub>2</sub> absorption capacities, with values of 344.15, 306.69, and 365.34 g·CO<sub>2</sub>/kg.absorbent h<sup>-1</sup> for the DEA, TEA, and AMP blends, respectively, with an improvement of 1–2 times. The blended alkanolamine absorbent demonstrated a high CO<sub>2</sub> absorption capacity in cycles 1, 2, and 3; however, its capacity gradually declined in cycle 4 of the DEA and AMP blends and cycle 5 of the TEA blend. The use of blended absorbents in multicycle IAM processes led to a reduction in the number of cycles, particularly when mixed with AMP, as DEA and TEA are derivatives of MEA [36]. At a concentration of 5 wt.%, the operation of 5 wt.% MEA required 2.8 h, as opposed to the 30 min–1 h duration required by the blended absorbents.

Furthermore, the correlation between the concentration of the blending component and the CO<sub>2</sub> absorption capacity over time was established by evaluating the amount of the absorbed CO<sub>2</sub> per unit of solvent. The viscosity of the absorbent, which is dependent on its concentration, played a vital role in controlling the absorption rate. A high viscosity of the absorbent resulted in a lower CO<sub>2</sub> absorption, as it impeded the diffusion of CO<sub>2</sub> gas molecules within the absorbent solution [48]. Therefore, the blended alkanolamine absorbent containing two amine components at a low concentration of 5 wt.% exhibited the highest CO<sub>2</sub> absorption capacity.



**Figure 2.** The CO<sub>2</sub> accumulation in the blended alkanolamine absorbents in each cycle of the multicycle integrated absorption–mineralization (IAM) was evaluated as a function of the absorption time for monoethanolamine (MEA)-blended (a) diethanolamine (DEA), (b) triethanolamine (TEA), and (c) aminomethyl propanol (AMP).

The present study aimed at investigating the impact of incorporating blended alkanolamine absorbents on the CO<sub>2</sub> absorption performance of MEA in multicycle IAM. The addition of DEA, TEA, and AMP at concentrations of 5, 10, and 15 wt.% to a constant 5 wt.% MEA led to a substantial improvement in CO<sub>2</sub> accumulation or CO<sub>2</sub> absorption capacity per unit of absorption time. We found that the optimal blend was 5 wt.% MEA and 5 wt.% of DEA, TEA, and AMP, as it improved the CO<sub>2</sub> absorption rate per unit of absorbent and decreased the viscosity of the solution. Furthermore, the results suggest AMP to be the most beneficial component among DEA, TEA, and AMP.

### 3.2. Characteristics of CO<sub>2</sub> Conversion

Herein, we investigated the potential for enhancing the generation of solid carbonates through the implementation of multicycle IAM using blended alkanolamine absorbents and high metal cation concentration brine waste [15–18,31]. The precipitation/regeneration process in multicycle IAM allows for the conversion of CO<sub>2</sub> gases into usable products through the precipitation of insoluble carbonates, followed by the auto-regeneration of the absorbent solution [22,23]. The optimization of the absorbent composition is important for achieving the maximum efficiency in the repeated cycles of the IAM process and converting the absorbed CO<sub>2</sub> into carbonates at a maximal quantity.

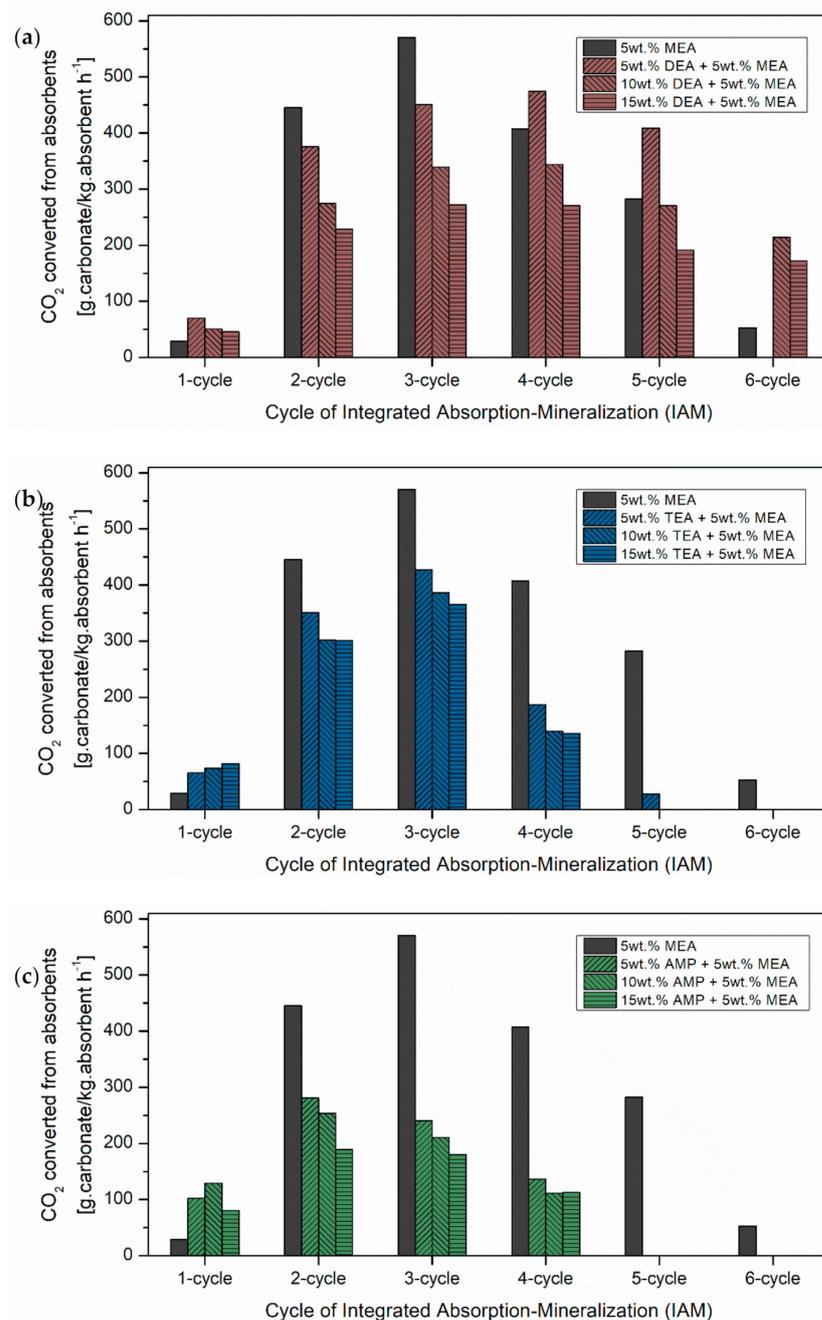
The multicycle IAM was studied to evaluate its potential in recovering the insoluble carbonate. This was accomplished through the optimization of the absorbent solution, composed of a constant 5 wt.% MEA and varying concentrations of DEA, TEA, and AMP at 5, 10, and 15 wt.%. The investigation aimed to assess the impact of blending these alkanolamines on the CO<sub>2</sub> conversion rate and the production of solid carbonates [51].

Figure 3 presents the amount of generated insoluble carbonates from the blended alkanolamine absorbents in the unit of grams of carbonate mixture per kilogram of blended absorbent per unit time. The results of the single 5 wt.% MEA absorbent served as references (gray columns) [23]. The investigation of the CO<sub>2</sub> conversion in multicycle IAM utilizing single and blended alkanolamine absorbents demonstrated that the trend of carbonate generation was consistent over time. The initial yield of CO<sub>2</sub> conversion was low, as a portion of the absorbed CO<sub>2</sub> molecules bonded with the amino groups in the amine absorbent during cycle 1. However, the addition of waste brine resulted in an increase in solid carbonate generation, leading to a corresponding improvement in the CO<sub>2</sub> conversion in subsequent cycles [22,23].

The results of the multicycle IAM study suggest that compared to a reference of 5 wt.% MEA, the blended alkanolamine absorbents, comprising a constant of 5 wt.% MEA and varying concentrations of DEA, TEA, and AMP at 5, 10, and 15 wt.%, demonstrated a lower conversion of CO<sub>2</sub> into solid carbonates over time. The amount of solid carbonate precipitated from the blended absorbent was lower than that from the reference solution, and compared to the addition of DEA and TEA in the MEA absorbents, the alkanolamine blends containing AMP exhibited a lower CO<sub>2</sub> conversion efficiency.

For example, in cycle 2, 444.97 g.carbonate/kg.absorbent h<sup>-1</sup> was recorded for the 5 wt.% MEA [23]. In contrast, the blended alkanolamine absorbents with a low concentration (5 wt.%) showed higher solid carbonate generation, with values of 375.59, 350.89, and 280.70 g.carbonate/kg.absorbent h<sup>-1</sup> for the DEA, TEA, and AMP blends, respectively. The blended alkanolamine absorbents incorporating TEA and AMP demonstrate a significant advantage in CO<sub>2</sub> absorption and accumulation owing to the stability of their chemical structures [38]. Nevertheless, this stability may also hinder the formation of solid precipitates through phase separation [37,38].

The multicycle IAM demonstrated a remarkable improvement in the recovery of solid carbonates from both the single and blended alkanolamine absorbents [22,23]. The results suggest that the blending components and concentrations of the absorbents play a crucial role in enhancing the solid carbonate production through repeated cycles of IAM. Compared to the reference, the alkanolamine blends consisting of a lower concentration of amine blending components with high CO<sub>2</sub> absorption capacities demonstrated greater solid carbonate generation. However, the preliminary results of the multicycle IAM process indicated a lower transformation rate of absorbed CO<sub>2</sub> into solid carbonates over time for the blended absorbents than for the 5 wt.% MEA single absorbent. A more detailed analysis of the effect of blending DEA, TEA, and AMP on the conversion efficiency of CO<sub>2</sub> is presented in Section 4.3.



**Figure 3.** The CO<sub>2</sub> conversion from blended alkanolamine absorbents in each cycle of multicycle integrated absorption–mineralization (IAM) was evaluated as a function of the absorption time for monoethanolamine (MEA)-blended (a) diethanolamine (DEA), (b) triethanolamine (TEA), and (c) aminomethyl propanol (AMP).

#### 4. Discussion

The present study aimed to enhance resource efficiency and improve carbon capture and utilization by evaluating the application of blended alkanolamine absorbents in CO<sub>2</sub> absorption and conversion [33–35,37]. The absorption behavior, conversion efficiency, and degradation efficiency of each blended absorbent were examined to optimize the multicycle IAM operation [22,23]. Parallel experiments were conducted using a single MEA absorbent under the same operating conditions to facilitate a comprehensive evaluation of the blended alkanolamine absorbents composed of DEA, TEA, and AMP in MEA [23]. The results of the study provide valuable insight into the effectiveness of utilizing blended absorbents

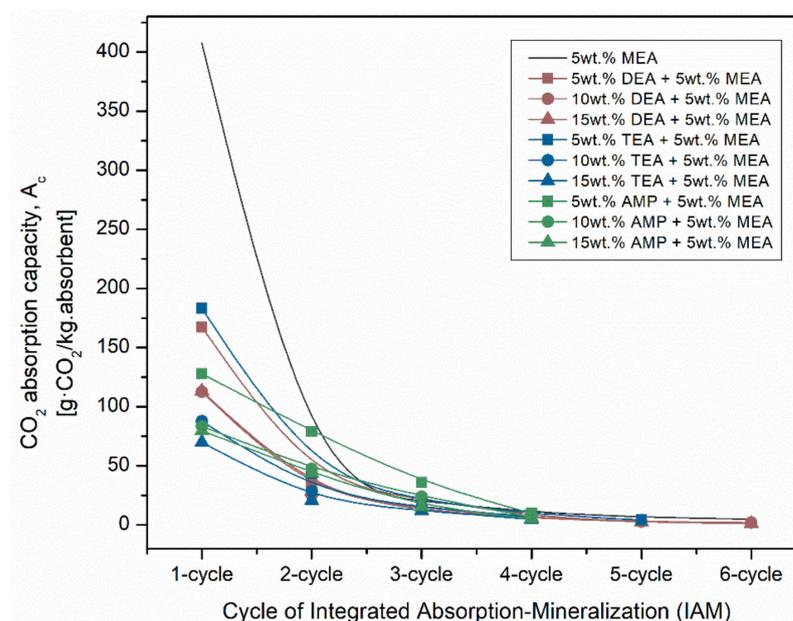
in multicycle IAM, ultimately contributing to the advancement of carbon capture and utilization technologies [13,15–18].

#### 4.1. Absorption Behavior

The development of blended alkanolamine absorbents is a critical aspect in the advancement of CO<sub>2</sub> capture and utilization in a multicycle IAM operation. These absorbents demonstrate potential application in various industrial processes and offer significant potential for improvement [33,36]. An alkanolamine blend consists of two key components: activator and promoter [36]. The activator enhances the CO<sub>2</sub> absorption rate, and the promoter increases the CO<sub>2</sub> absorption capacity. Compared to that in a single MEA absorbent [23], the ability to modify the components and their concentrations in the blended absorbents enables the optimization of the CO<sub>2</sub> absorption over the operation time.

The blended alkanolamine absorbents were synthesized by including two amine components with a constant 5 wt.% MEA, varying the second amine component as DEA, TEA, or AMP, as well as the concentrations of the second amine component at 5, 10, and 15 wt.%. The aim of blending the alkanolamine absorbents was to observe the change in the CO<sub>2</sub> absorption behavior compared to that in the original MEA absorbent. The variations in the amine composition and concentration were expected to have a remarkable impact on the CO<sub>2</sub> absorption properties of the blended absorbents [37,38].

Figure 4 demonstrates the CO<sub>2</sub> absorption capacity of both the single 5 wt.% MEA absorbent and the blended absorbent across multicycle IAM. The CO<sub>2</sub> absorption capacity was calculated using Equation (6), which provided a quantitative measure of the capture CO<sub>2</sub> ability of the absorbent from the flue gas and, thus, the CO<sub>2</sub> capture performance of each absorbent during repeated cycles in the IAM process [48].



**Figure 4.** CO<sub>2</sub> absorption capacity of blended alkanolamine absorbents in multicycle integrated absorption–mineralization (IAM).

The results from the analysis of the blended absorbents of DEA, TEA, and AMP, each with a concentration of 5 wt.%, in combination with 5 wt.% MEA, revealed that the CO<sub>2</sub> absorption capacities were lower in comparison to that of the 5 wt.% MEA absorbent. The CO<sub>2</sub> absorption capacities were determined to be 234.96, 260.17, and 252.61 g·CO<sub>2</sub>/kg. absorbent for the DEA-, TEA-, and AMP-blended absorbents, respectively, whereas the 5 wt.% MEA absorbent demonstrated a CO<sub>2</sub> absorption capacity of 481.30 g·CO<sub>2</sub>/kg. absorbent [23]. Notably, none of the amine components showed a promoting effect when blended with the MEA.

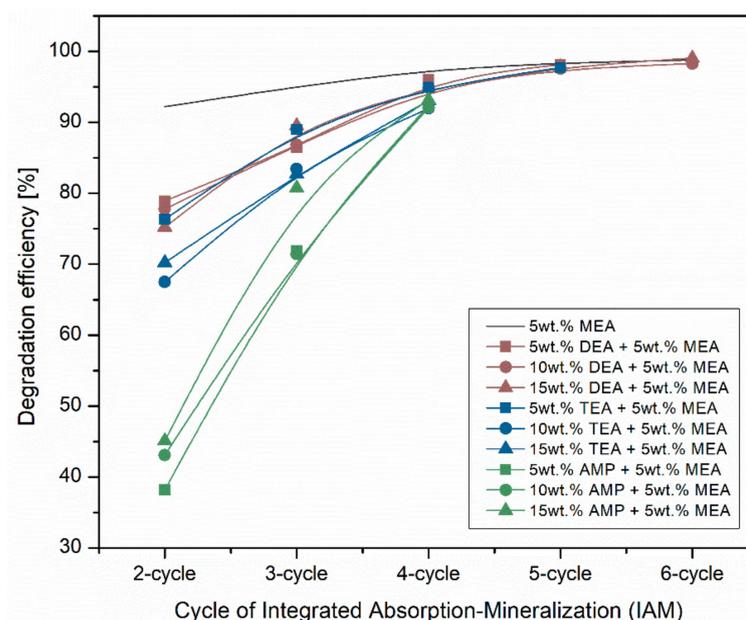
The blended absorbents demonstrated a positive impact on the CO<sub>2</sub> absorption capacity over the operation time and the CO<sub>2</sub> absorption rate. Particularly, the blend of 5 wt.% AMP in the MEA absorbent resulted in a substantial improvement, as indicated in Figure 2. Compared to the other blended absorbents, this blend achieved the highest CO<sub>2</sub> absorption capacity per unit of time, up to two times higher in each cycle. These results suggest that the AMP component acted as a promoter for the single alkanolamine absorbent when blended at low concentrations in MEA. The application of DEA, TEA, and AMP in the blended absorbents demonstrates a potential to enhance the CO<sub>2</sub> absorption rate, because their low CO<sub>2</sub> absorption kinetics may lead to a reduction in the reaction time, thus increasing the effectiveness of the absorbent–CO<sub>2</sub> interaction [39–41].

#### 4.2. Degradation Efficiency

The utilization of blended alkanolamine absorbents through the repetition of multicycle IAM was investigated to maximize the recovery of CO<sub>2</sub> absorption and conversion [22,23]. During operation, the aqueous alkanolamine absorbent interacts with flue gas, resulting in unwanted oxidative reactions and other chemical reactions. These reactions lead to the loss of amine molecules in solvent through the conversion of amines to other substances. The formation of free radicals, such as oxidized hydrogen atoms in the amino group, contributes to the degradation of the absorbent, which results in a decrease in the CO<sub>2</sub> absorption capacity of both single and blended alkanolamine absorbents owing to oxidation and thermal degradation [51–54]. To mitigate the absorbent's degradation, the approach of utilizing a blend of two amine components was employed [33–35,37]. The degradation efficiency was calculated by determining the mechanism of absorbent degradation, as shown in Equation (7).

Figure 4 demonstrates that the initial capacity of the fresh absorbent to absorb CO<sub>2</sub> was the highest in the first cycle. It was anticipated that the degradation of the absorbent would not be significant. The capacity of the recycled absorbent to absorb CO<sub>2</sub> was inversely proportional to its degradation in subsequent cycles.

Figure 5 presents the degradation efficiency of each blended alkanolamine absorbent during the IAM cycle. A degradation ability of an absorbent approaching 100% means that the capacity to absorb CO<sub>2</sub> has been eliminated. Therefore, an absorbent that can be used in the IAM cycle more than once should demonstrate little degradation after the first cycle.



**Figure 5.** Degradation efficiency of blended alkanolamine absorbents in multicycle integrated absorption–mineralization (IAM).

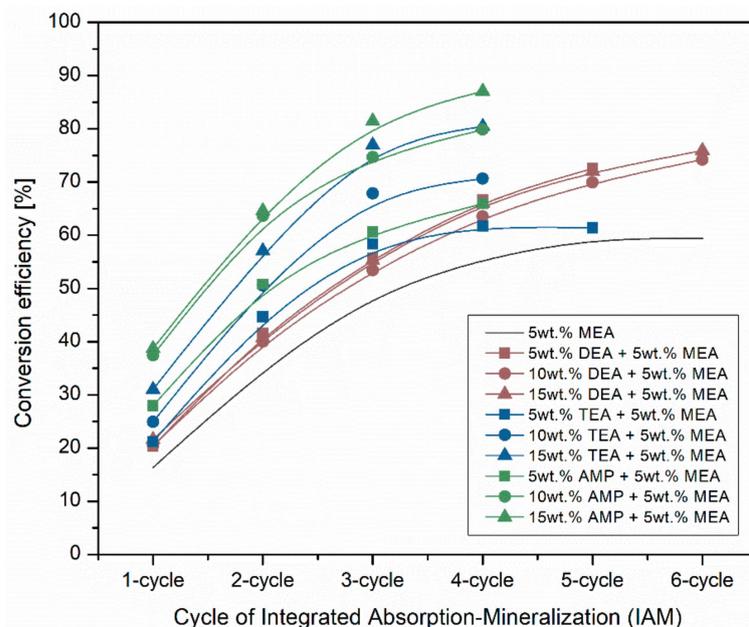
The addition of DEA, TEA, and AMP into MEA blends at various concentrations demonstrated a substantial improvement in the loss performance of the single 5 wt.% MEA absorbent. The results revealed that compared to the initial degradation efficiency of 92.22% in the single MEA absorbent [23], these blended absorbents demonstrated a decrease in the degradation efficiency, ranging from 14.44% to 58.59%. The impact of blending concentrations on the degradation efficiency was not consistent across all absorbents, with lower concentrations of DEA, TEA, and AMP having the potential to mitigate absorbent degradation.

The MEA-based blended solvents with DEA, TEA, and AMP components demonstrated a reduced overall CO<sub>2</sub> absorption kinetics for the blends, exhibiting an improvement in the CO<sub>2</sub> absorption rate. This was attributed to the absorbent's ability to absorb larger amounts of CO<sub>2</sub> per unit of absorbent, resulting in a lower absorbent degradation [39–41]. The composition and proportion of the alkanolamine blend played a critical role in determining the absorption behavior and degradation performance of the absorbent [33].

#### 4.3. Conversion Efficiency

The process of transforming absorbed CO<sub>2</sub> emissions into carbonates is referred to as CO<sub>2</sub> conversion. Herein, we aimed to optimize the generation of carbonate through the precipitation of the absorbed CO<sub>2</sub> in the absorbent. The optimal composition and concentration of the blended alkanolamine absorbents enhanced the performance of the multicycle IAM in terms of CO<sub>2</sub> conversion. The conversion efficiency, which quantifies the amount of absorbed CO<sub>2</sub> transformed into solid carbonates [51], was determined using Equation (8).

The CO<sub>2</sub> conversion and utilization form an important aspect of carbon management. Therefore, the conversion efficiency of solid carbonate production is related to the amount of CO<sub>2</sub> absorbed. Figure 6 presents the trend of the conversion efficiency of blended alkanolamines as absorbents in the production of solid carbonates. The study results showed a promising increase in the CO<sub>2</sub> conversion efficiency for the blended alkanolamines over subsequent cycles.



**Figure 6.** Conversion efficiency of blended alkanolamine absorbents in multicycle integrated absorption–mineralization (IAM).

The results of the repeated multicycle IAM process showed a substantial enhancement in the formation of precipitated carbonates. The combination of MEA with varying concentrations of DEA, TEA, and AMP components at 5, 10, and 15 wt.%, respectively,

demonstrated a considerable improvement in the conversion of absorbed CO<sub>2</sub> into solid carbonates. Compared to the reference 5 wt.% MEA absorbent that demonstrated a conversion efficiency of 59.42%, the blended absorbents exhibited an increase in the conversion efficiency up to 46.55% [23]. The effect of varying the concentration of the DEA, TEA, and AMP components in the blended absorbents on the conversion efficiency was consistent with the trend observed in the single MEA absorbent. The higher blending concentrations in the blends exhibit the potential to recover the generation of precipitated carbonates.

Particularly, the AMP component in the blended alkanolamine absorbents demonstrated a higher conversion efficiency than other components. AMP, with a distinctive chemical structure featuring locked amino groups, demonstrated an enhanced selectivity towards CO<sub>2</sub> relative to the absorbent [38]. Consequently, incorporating AMP in MEA solvent has the potential to enhance CO<sub>2</sub> conversion in blended absorbent systems.

#### 4.4. Optimization of Multicycle IAM Operation

The optimization of the absorbent in multicycle IAM involves determining the best alkanolamine blend of component and concentration that maximizes CO<sub>2</sub> conversion while minimizing degradation efficiency. It can be accomplished through experimentation and data analysis of the absorbent behavior in repeated cycles of absorption, precipitation/regeneration, and preparation. The optimal absorbent should exhibit an efficient CO<sub>2</sub> conversion into solid carbonates and low degradation efficiency. Moreover, the best blending component and concentration in the blended alkanolamine absorbent can be adjusted according to the industrial application requirements [33–37]. The criteria for selecting the appropriate alkanolamine absorbent in multicycle IAM depend on the CO<sub>2</sub> absorption capacity, conversion efficiency, absorbent degradation, toxicity, and cost, as per Equation (9).

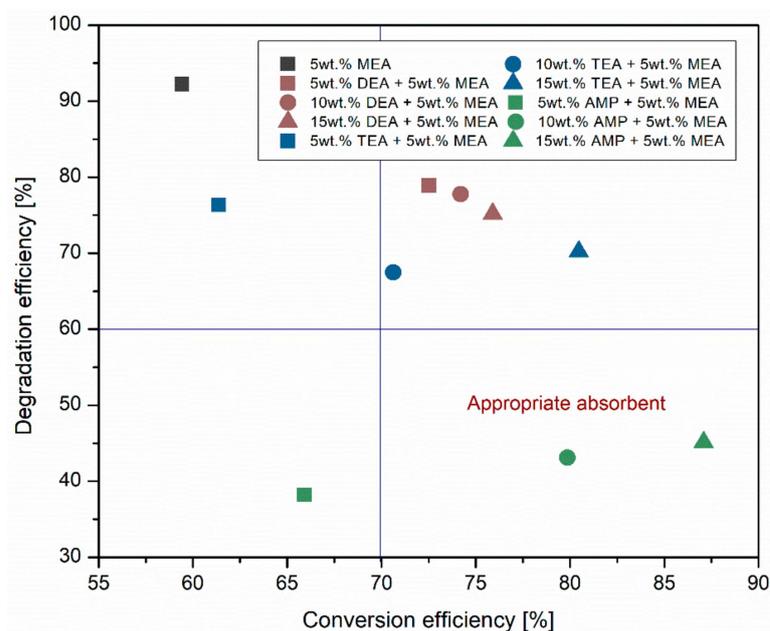
$$\begin{aligned} \text{Appropriate blended absorbent} = & (W_1 \times \text{CO}_2 \text{ absorption factor}) + \\ & (W_2 \times \text{Conversion factor}) + (W_3 \times \text{Degradation factor}) \\ & + (W_4 \times \text{Toxic factor}) + (W_5 \times \text{Cost factor}) \end{aligned} \quad (9)$$

The CO<sub>2</sub> absorption factor represents the fraction of the blended alkanolamine absorbent's actual CO<sub>2</sub> absorption capacity to its nominal CO<sub>2</sub> absorption capacity [48]. The degradation factor accounts for the degradation of the amine solution over time due to the fact of chemical reactions and impurities [52–54] and can be estimated using Equation (7). The conversion factor represents the fraction of CO<sub>2</sub> that is converted into a stable carbonate after absorption [51] and can be estimated using Equation (8). The toxic factor indicates the level of harm posed to humans [59,60], while the cost factor represents the cost of the amine solution [61–63]. W<sub>1</sub>, W<sub>2</sub>, W<sub>3</sub>, W<sub>4</sub>, and W<sub>5</sub> are weights assigned to each variable. These factors range from 0 to 1, with 0 indicating no effect and 1 indicating the greatest effect.

A composite index can be obtained by multiplying these factors, which can be used to optimize the blending concentration of different types of amine components and to select the most appropriate alkanolamine absorbent for multicycle IAM. However, this evaluation must be based on achieving a conversion efficiency greater than 70% [55–59] and a degradation efficiency lower than 60% [23], since conversion and degradation efficiencies are of primary importance in multicycle IAM.

Figure 7 demonstrates a comprehensive evaluation of the performance of various blended alkanolamine absorbents in multicycle IAM, illustrating the effectiveness of each blended absorbent in terms of the conversion efficiency and absorbent degradation. The results indicate that of the two blended absorbents evaluated, only a few selected ones exhibited the optimal balance of CO<sub>2</sub> conversion and minimal absorbent degradation [33,37]. The conversion efficiency of these blends is of crucial importance, as it directly impacts the overall efficiency of the multicycle IAM process [51]. Moreover, the absorbent degradation requires a key consideration, as it affects the longevity and sustainability of the absorbent in long-term operation [51–54]. Therefore, the blended absorbents that closely meet the basis of conversion and degradation efficiencies are the most suitable for further optimization

and implementation in multicycle IAM, classifying the region where conversion efficiency is increased beyond 70% and degradation efficiency is decreased below 60%.



**Figure 7.** Correlation between conversion and degradation efficiencies in blended alkanolamine absorbents in multicycle integrated absorption–mineralization (IAM).

The selection of appropriate blended alkanolamine absorbents for operating multicycle IAM is crucial in maximizing the benefits of high CO<sub>2</sub> absorption and conversion per operation time, low degradation rate, low toxicity, and cost efficiency. Among various alkanolamine blends, the addition of 15 wt.% AMP to a constant 5 wt.% MEA showed the highest composite index (Table S1), resulting in the highest CO<sub>2</sub> absorption rate of 153.93 g·CO<sub>2</sub>/kg·absorbent h<sup>-1</sup> and carbonate production rate of 134.04 g·carbonate/kg·absorbent h<sup>-1</sup> over a relatively short overall operation time of 43.17 min at the end of the multicycle. This blended absorbent exhibited a low degree of degradation at 45.12% and a high CO<sub>2</sub> conversion efficiency of 87.08%, which were the main focus of this study.

Blending alkanolamine absorbents is a widely used approach to improve the CO<sub>2</sub> absorption while simultaneously reducing absorbent degradation, toxicity, and cost. This approach is specifically aimed at improving the absorption section in multicycle IAM. The amine components commonly used for blending with MEA to enhance CO<sub>2</sub> capture and conversion and inhibit absorbent degradation are DEA, TEA, and AMP. The addition of these blending components slows the rate of absorbent degradation and extends the conversion of CO<sub>2</sub> absorption. Consequently, this leads to an increased CO<sub>2</sub>-absorbent selectivity, resulting in a higher CO<sub>2</sub> conversion efficiency and reduced absorbent degradation. The addition of 15 wt.% AMP to a constant 5 wt.% MEA showed the highest composite index compared to the single MEA [23] and all of the other blended solutions. Furthermore, this blended absorbent achieved a conversion efficiency greater than 70% [55–58] and a degradation efficiency lower than 60% [23], which are crucial factors in operating against multicycle IAM. Thus, blending alkanolamine absorbents is a promising approach for achieving efficient and sustainable multicycle IAM, and the selection of appropriate blending components is critical for optimizing the process performance.

## 5. Conclusions

Blended alkanolamine absorbents have been proposed as a more sustainable solution for CCUS technology due to the potential environmental concerns associated with the exclusive use of MEA absorbent. The use of MEA absorbent for large-quantity CO<sub>2</sub>

removal has raised environmental concerns due to the fact of its high-energy consumption and erosiveness [19,22]. MEA absorbent is prone to oxidative and thermal degradation, which can reduce the efficiency of the CO<sub>2</sub> capture process [28,54,64]. Therefore, blended alkanolamine absorbents offer a more sustainable solution for CCUS technology by overcoming the limitations associated with the exclusive use of MEA absorbent [23]. The behavior of blended absorbents is influenced by the composition and concentration of the amine component. The parameters associated with blended absorbents, such as the CO<sub>2</sub> absorption capacity and rate, carbonate generation, CO<sub>2</sub> conversion, absorbent degradation, and operation time, were optimized through repeated cycles of absorption, precipitation/regeneration, and preparation. The alkanolamine blends adjusted the amine component and concentration, leading to improved performance in terms of the CO<sub>2</sub> removal and sustainability [33–37].

The blended alkanolamine absorbents consisting of different concentrations (5, 10, and 15 wt.%) of DEA, TEA, and AMP components in a constant 5 wt.% MEA solution mitigated the shortcomings associated with using an MEA absorbent alone. These blended solvents also enhanced the CO<sub>2</sub> absorption rate, conversion efficiency, degradation efficiency, and operation time under similar temperature and pressure conditions (20–25 °C and 1 atm). The optimization of the amine blending composition and concentration affected the absorption behavior and rate and conversion and degradation efficiencies, which can be further investigated through the multicycle IAM.

The AMP absorbent was the most effective component in the MEA-based absorbent, followed by DEA and TEA absorbents. Therefore, the addition of AMP in MEA solvent resulted in a substantial improvement in both CO<sub>2</sub> conversion and absorbent degradation, as well as an increase in the rate of CO<sub>2</sub> absorption. However, low concentrations of AMP in the MEA blends positively impacted the rate of CO<sub>2</sub> absorption and conversion, whereas high concentrations strongly impacted the amount of CO<sub>2</sub> absorption capacity and absorbent degradation. Among the examined amine blending components, the AMP component exhibited the highest promoting effect on the absorption efficiency of the MEA absorbent.

Additionally, the kinetic behavior of the CO<sub>2</sub> absorption in the individual blend components can be utilized to predict the behavior of blended alkanolamine absorbents [39–41]. For instance, the incorporation of AMP as an amine component in MEA-based blended absorbents results in an increase in CO<sub>2</sub> accumulation per unit of time and absorbent degradation owing to its slower CO<sub>2</sub> absorption kinetic, which in turn lowers the overall kinetic of the blend. The interaction between the absorbent and CO<sub>2</sub> may be heightened, as the contact time between the two is prolonged. Hence, the loss of amine molecules during the CO<sub>2</sub> absorption also recovers.

The results suggest that the optimal alkanolamine absorbent in multicycle IAM involves the combination of 15 wt.% AMP and a constant 5 wt.% MEA blend, meeting the highest composite index and the selection criteria of a conversion efficiency greater than 70% and a degradation efficiency lower than 60%, providing excellent performance in multicycle IAM in terms of both CO<sub>2</sub> absorption capacity and carbonate generation over the total operation time. The utilization of the proposed blended absorbent in the multicycle IAM produced promising results, with a conversion efficiency of 87.08%. This blend absorbed 144.52 g of CO<sub>2</sub> per kilogram of absorbent and produced 125.85 g of carbonates per kilogram over the course of four cycles, which were completed in 43.17 min. The degradation efficiency of this blend was 45.12%, which is considered to be acceptable in this context. The use of a single MEA absorbent in multicycle IAM could be replaced with blended alkanolamine absorbents, as they offer improved CO<sub>2</sub> absorption and utilization and reduced absorbent degradation. The blended absorbents exhibit durability and effectiveness in repeated cycles, leading to an increased CO<sub>2</sub> absorption and carbonate precipitation while maintaining a balance of absorbent degradation and reducing the overall operation time.

Multicycle IAM using blended alkanolamine absorbents offers a more sustainable solution for CCUS technology compared to MEA absorbent alone. The blended solvents

improve the CO<sub>2</sub> absorption capacity and rate, conversion efficiency, degradation efficiency, and operation time. The addition of AMP in MEA solvent substantially improves CO<sub>2</sub> conversion and absorbent degradation, resulting in an increased rate of CO<sub>2</sub> absorption. The optimal alkanolamine absorbent involves the combination of 15 wt.% AMP and a constant 5 wt.% MEA blend, providing excellent performance in terms of both conversion and degradation efficiencies over the total operation time. The utilization of the proposed blended absorbent in multicycle IAM produced promising results, with a conversion efficiency of 87.08% and reduced absorbent degradation of 45.12%. The experimental results of the blended absorbents demonstrate their effectiveness in terms of conversion and degradation efficiencies, making them suitable for implementation in multicycle IAM for industrial applications. Future research can focus on further optimizing the amine blending composition and concentration and investigating their long-term performance and economic feasibility.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13040487/s1>, Table S1: Composite index of blended alkanolamine absorbent in multicycle IAM.

**Author Contributions:** Conceptualization, C.T. and S.T.; methodology, C.T.; software, C.T.; validation, C.T. and S.T.; formal analysis, C.T.; investigation, C.T. and S.T.; resources, C.T. and S.T.; data curation, C.T.; writing—original draft preparation, C.T.; writing—review and editing, C.T. and S.T.; visualization, C.T.; supervision, S.T.; project administration, C.T.; funding acquisition, S.T. All authors have read and agreed to the published version of the manuscript.

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