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Chapter 4

# Emerging New Types of Absorbents for Postcombustion Carbon Capture

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Additional information is available at the end of the chapter

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**Abstract**

Carbon capture is the most probable technology in combating anthropogenic increase of $CO_2$ in the atmosphere. Works on developing emerging absorbents for improving carbon capture performance and reducing process energy consumption are actively going on. The most worked-on emerging absorbents, including liquid-liquid biphasic, liquid-solid biphasic, enzymatic, and encapsulated absorbents, already show encouraging results in improved energy efficiency, enhanced $CO_2$ absorption kinetics, increased cyclic $CO_2$ loading, or reduced regeneration temperature. In this chapter, the latest research and development progress of these emerging absorbents are reviewed along with the future directions in moving these technologies to higher-technology readiness levels.

**Keywords:** postcombustion capture, biphasic absorbent, lipophilic amine, ionic liquids, amino acids, enzymes, encapsulated

## 1. Introduction

Postcombustion carbon capture is considered one of the most promising and feasible technologies for reducing carbon dioxide ($CO_2$) emissions from energy-intensive industries such as coal-fired power plants. This is because postcombustion carbon capture has relatively higher level of technology readiness, lower energy penalty, and favorable cost compared to other carbon capture technologies (e.g., oxy-fuel, integrated gasification combined cycle or IGCC) [1]. Conventional aqueous alkanolamine-based carbon capture adsorbents were developed over half a century ago for natural gas/$CO_2$ separation as well as syngas/$CO_2$ separation, both work

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at high absorption pressures. Research work has been conducted to extend the conventional absorbents for coal-fired power plant $CO_2$ capture. These are classified as first-generation absorbents [2]. However, for the application of coal-fired power plant $CO_2$ capture, the flue gas is at about ambient atmosphere. This difference of the $CO_2$ absorption operation pressure makes the first-generation absorbents not satisfactory. Among the traditional alkanolamines, 30 wt% monoethanolamine (MEA) with a cyclic $CO_2$ loading of 4–5 wt% and a regeneration temperature of about 120°C is regarded as a benchmark absorbent [3]. In a continuous operation, a huge volume of the liquid absorbent has to be pumped back and forth between the absorber and the stripper during absorption and regeneration. For regeneration, a significant amount of water in the absorbent (an aqueous solution of MEA) is vaporized in the regenerator to flow upward acting as both a heat transfer agent and a stripping gas. The energy penalty of the regeneration could be as high as 4.2 GJ/t$CO_2$ [4]. The power generation efficiency would be reduced by about eight percentage points from a range of 28–34% to 20–26%. Therefore, research efforts are continuing in the hope to improve carbon capture performance and to reduce energy penalties. As the third-generation absorbents [2] (second generation: demonstration in 2020–2025 time frame; third generation: at early development stage), biphasic absorbents (liquid-liquid as well as liquid-solid phase change), enzymatic-enhanced, and encapsulated absorbents are attracting ever increasing research interest [5–8].

This chapter presents a review on these emerging absorbents and identifies directions for further research at pilot scale and beyond. We will examine the achievement on the $CO_2$ absorption energy efficiency, enhanced $CO_2$ absorption kinetics, and increased cyclic $CO_2$ loading or lower regeneration temperature.

## 2. Liquid-liquid biphasic absorbent systems

Liquid-liquid biphasic absorbent systems generally have one liquid phase fed into an absorber while upon $CO_2$ absorption or increase of temperature, the absorbent turns into two immiscible liquid phases (one $CO_2$-rich and the other $CO_2$-lean phases) [9, 10]. Because of the separation of the two liquid phases, during regeneration, only the $CO_2$-rich phase, a smaller flow than in a conventional alkanolamine case, is sent to the stripper/regenerator. The $CO_2$-lean phase is mixed with the regenerated stream (now in lean state) and sent back to the absorber to perform another round of $CO_2$ absorption. By doing so, the regeneration heat consumption can be drastically reduced and therefore, compared to the conventional postcombustion carbon capture absorbents, biphasic absorbent systems may reduce energy consumption and capital cost (requiring relatively smaller strippers).

It is found that, up to 2016, the active developers of the liquid-liquid biphasic absorbents are 3H Company, IFP Energies nouvelles, Korea Institute of Energy Research, Norwegian University of Technology, Tsinghua University, and University of Dortmund. In August 2015, DOE approved and funded 16 transformative carbon capture projects, two of which were on biphasic absorbents [11]. It is likely that more biphasic absorbent work will be published in the next few years.

### 2.1. Mechanism of liquid-liquid phase separation

The solubility or liquid-liquid phase separation in aqueous amine systems is determined by the relative strength of the molecular interactions among the amine molecules, among the water molecules, and between the amine and the water molecules [12, 13]; nonaqueous liquid-liquid biphasic absorbent would follow the same principle. For instance, in a system of pentane and water, the interaction of pentane with water is weaker than the interaction among water molecules, and therefore pentane does not dissolve well in water. By contrast, in a system of ethanol and water, the interaction of ethanol and water is stronger than the interaction among ethanol molecules and as a result ethanol dissolves well in water. The relative strength of the molecular interactions is known to be influenced by temperature, and change in temperature could turn on a liquid-liquid phase separation from a homogeneous solution, or vice versa, i.e., two liquid phases merging into one homogeneous liquid phase [9]. The possibilities of solubility or phase separation are summarized in **Figure 1** [12, 14]. The real situation of an amine and water could be complicated. Only systems with a lower critical solution temperature (LCST, case C) and both upper critical solution temperature (UCST) and LCST (case B), are potentially suitable for phase separation absorbents. When temperature is increased to above LCST, by breakdown of strong cohesive interactions between the solute and solvent [15], a homogeneous solution changes into two immiscible liquid phases (cases B and C in **Figure 1**). Since postcombustion carbon capture is operated at about 40°C, the LCST of a phase separation absorbent should be higher than the absorption temperature. When $CO_2$ is absorbed, new chemical species (e.g., carbamate, protonated amine, and carbonate and/or bicarbonate ions) are formed. These new species may lower the LCST of the system and result in phase separation at CO2 absorption temperature.

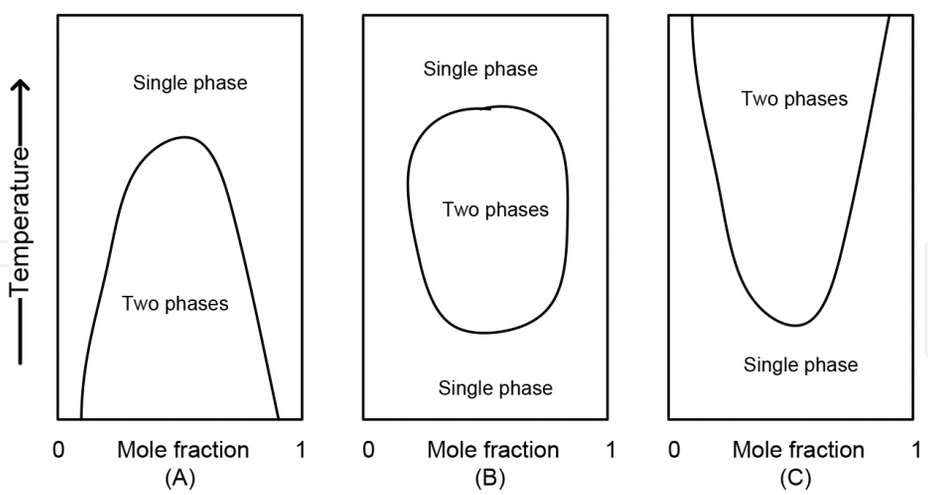


**Figure 1.** Partial miscibility curves of binary liquid-liquid mixtures. (A) UCST; (B) UCST, and LCST; (C) LCST [15].

### 2.2. Nonaqueous liquid-liquid biphasic absorbents

3H Company filed seven patents on nonaqueous solution of amine dissolved in an alcohol as self-concentrating absorbents [16]. The amines described in their patents include alamine 336,

dibutylamine, diethanolamine (DEA), diisopropylamine, MEA, and piperazine, and the alcohols used as solvents include decylalcohol and isooctanol. Yeo Il Yoon's group at the Korea Institute of Energy Research reported a study on absorbent systems of MEA, DEA (diethanolamine) in 1-heptanol, 1-octanol, and isooctanol [17]. They found that, using a bubbling tube at 40°C with 30% $CO_2$ in $N_2$, the absorbent changed into two immiscible liquid phases when $CO_2$ was absorbed. The $CO_2$-rich phase was found to be dominant with amine-bonded $CO_2$ and unreacted amine, while the $CO_2$-lean phase was mainly alcohol with a small amount of free amine. Proton nuclear magnetic resonance ($^1$H NMR) characterization further showed that MEA or DEA carbamate and protonated amines existed in the rich phase, possibly in ion pairs such as $MEACOO^-MEAH^+$.

In one of Hu's studies, the $CO_2$-rich phase had a $CO_2$ loading of about 27 wt% with a volume only about 30% of the aqueous MEA case [18]. A batch mode of the rich phase stripping of a nonaqueous biphasic absorbent at 115–125°C indicated deeper regenerability down to about 90% of the absorbed $CO_2$ compared with that of the aqueous MEA absorbent, a regeneration of about 50%. In Hu's study, the regenerated stream, now mainly MEA, was combined with the lean stream (mainly alcohol) and sent back to the absorber. Therefore, the potential net cyclic $CO_2$ loading (the ratio of the weight of $CO_2$ released in regeneration to the weight of the absorbent) would double that of the aqueous amine absorbent, and by regenerating the $CO_2$-rich phase only (a much smaller volume compared to the whole absorbent), less thermal energy consumption and a smaller stripper are expected.

In Hu's study of biphasic absorbents [18], the boiling points of the alcohols were within 176–195°C, which was higher than the regeneration temperature and the alcohols did not evaporate. Improvements could be made by applying, e.g., a stream of $CO_2$ from the regenerator as a stripping gas, using a much smaller reboiler to raise the temperature of this $CO_2$ stream 20–30°C higher than the regeneration temperature, and feeding the gas directly into the regenerator. Meanwhile, the energy efficiency of the self-concentrating systems should be examined and compared with the conventional MEA technology.

In addition, in these biphasic absorbent systems, the absorbents are nonaqueous and likely will absorb the moistures from flue gases and may cause potential problems including mutual dissolution amongst amine-alcohol-water and may need for water separation. The relatively high viscosity of the absorbents is another concern; the viscosity of alcohol amine absorbents was found to increase upon $CO_2$ absorption [10].

### 2.3. Aqueous liquid-liquid biphasic absorbents

There are more works reported on aqueous liquid-liquid biphasic absorbents. A group from the University of Dortmund theoretically analyzed the solubility of liquid lipophilic amines in water. Different from the hydroxyl group-bearing conventional alkanolamines, lipophilic amines have relatively lower solubility in water. The amines screened are listed in **Table 1** [12, 13], tested either alone or mixed.

| Type | Chemical | Abbreviation | Molar mass |
|---|---|---|---|
| Chain amines | Hexylamine | HA | 101.19 |
| | Heptylamine | HpA | 115.22 |
| | Octylamine | OtA | 129.24 |
| | Di-n-propylamine | DPA | 101.19 |
| | Diisopropylamine | DIPA | 101.19 |
| | Di-n-butylamine | DBA | 129.24 |
| | Diisobutylamine | DIBA | 129.24 |
| | Di-sec-butylamine | DsBA (B1) | 129.24 |
| | N-sec-Butyl-n-propylamine | SBPA | 115.22 |
| | N,N-Diisopropylmethylamine | DIMA | 115.22 |
| | N,N-Diisopropylethylamine | DIEA | 129.24 |
| | N,N-Dimethylbutylamine | DMBA | 101.19 |
| | N,N-Dimethyloctylamine | DMOA | 157.3 |
| Cycloalkylamines | Cyclohexylamine | CHA | 99.17 |
| | Cycloheptylamine | CHpA | 113.2 |
| | Cyclooctylamine | COA | 127.23 |
| | 2-Methylcyclohexylamine | 2MCA | 113.2 |
| | N-Methylcyclohexylamine | MCA (A1) | 113.2 |
| | N-Ethylcyclohexylamine | ECA | 127.23 |
| | N-Isopropylcyclohexylamine | IPCA | 141.25 |
| | N,N-Dimethylcyclohexylamine | DMCA | 127.23 |
| | N,N-Diethylcyclohexylamine | DECA | 155.28 |
| | Dicyclohexylamine | DCA | 181.32 |
| Aromatic amines | Benzylamine | BzA | 107.15 |
| | N-Methylbenzylamine | MBzA | 121.18 |
| | N-Ethylbenzylamine | EBzA | 135.21 |
| | N-Isopropylbenzylamine | IPBzA | 149.23 |
| | Phenylethylamine | PhEA | 121.18 |
| | N,N-Dimethylbenzylamine | DMBzA | 135.21 |
| Cyclic amines | 2,6-Dimethylpiperidine | 2,6-DMPD | 113.2 |
| | 3,5-Dimethylpiperidine | 3,5-DMPD | 113.2 |
| | 2-Methylpiperidine | 2MPD | 99.17 |
| | 2-Ethylpiperidine | 2EPD | 113.2 |
| | 2,2,6,6-Tetramethylpiperidine | TMPD | 141.25 |

| Type | Chemical | Abbreviation | Molar mass |
|---|---|---|---|
| | N-Methylpiperidine | MPD | 99.17 |
| | N-Ethylpiperidine | EPD | 113.2 |
| Other amines | Monoethanolamine | MEA | 61.08 |
| | N-Methyldiethanolamine | MDEA | 119.16 |
| | 2-Amino-2-methyl-1-propanol | AMP | 89.14 |
| | 2-Amino-2-methyl-1,3-propanediol | AMPD | 105.14 |
| | N,N,N′,N′-Tetramethyl-1,6-hexanediami | TMHDA | 172.31 |
| | N-Methylmorpholine | MMP | 101.15 |
| | N,N-dimethyl-1,3-propanediamine | DMPDA | 102.18 |
| | Piperazine | pZ | 86.14 |

**Table 1.** Lipophilic amines screened in the University of Dortmund's study [9, 12, 13].

Among the lipophilic amines tested, no candidates were found to be suitable as liquid-liquid phase separation absorbents because of their low $CO_2$ loading, lack of phase separation, or, complicated phase change behaviors or solid precipitation upon $CO_2$ absorption. By mixing two different amines (the so-called bi-amine systems), however, would enable a $CO_2$ capture performance that neither of the two components would show alone, such as phase separation, because the physical and chemical properties of the two components may supplement each other. In many cases, one (the so-called activator) of the two amine components has a relatively higher $CO_2$ absorption capacity and the other one (the so-called promoter) functions to improve phase separation and/or to enhance reaction rates of absorption or regeneration. Two mixtures (i.e., MCA-DSBA and DPA-DMCA) with a ratio of 3:1 have been identified at an optimum total concentration of 3-4 M (**Table 1**). The $CO_2$ absorption isotherms of these two mixtures were evaluated and compared with those of aqueous MEA [12]. At 40°C (the typical postcombustion capture temperature), both MCA-DSBA and DPA-DMCA were found to have higher $CO_2$ loadings compared to MEA (**Figure 2**). Due to its favorable $CO_2$ absorption isotherm, MCA-DSBA performed a little more superior to DPA-DMCA. By contrast, at 65–70°C (could be used as regeneration temperature), the two mixture systems had much lower $CO_2$ loading than MEA (even at 120°C). This indicated that the cyclic loading of these mixture systems may reach about 10 wt% at a lower regeneration temperature of 65–70°C and could double the cyclic loading of MEA at 120°C. Therefore, the bi-amine systems may have the potential to achieve better regeneration (up to 90%).

Besides the two-component bi-amine mixtures, three-component mixtures can also be developed. Since some aqueous lipophilic amines have LCST lower than 40°C, the absorbent could be in two liquid phases before $CO_2$ absorption takes place. A solubilizer could be added to increase the LCST. One of the examples is DMCA-MCA-AMP in a ratio of 3:1:1 (see **Table 1**), where AMP was used as a solubilizer to increase the LCST (to > 40°C) of DMCA-MCA [13]. It was found that the $CO_2$ loading of DMCA-MCA-AMP was 3 mol/L (ca. 13.2 wt %) at 40°C and at a $CO_2$ partial pressure of 0.15 bar and, at 75°C, over 90% of $CO_2$ was regen-

erated. Therefore, it seems that the addition of AMP led to the increase of LCST about 15–20°C but without impairing the $CO_2$ absorption and desorption performance.

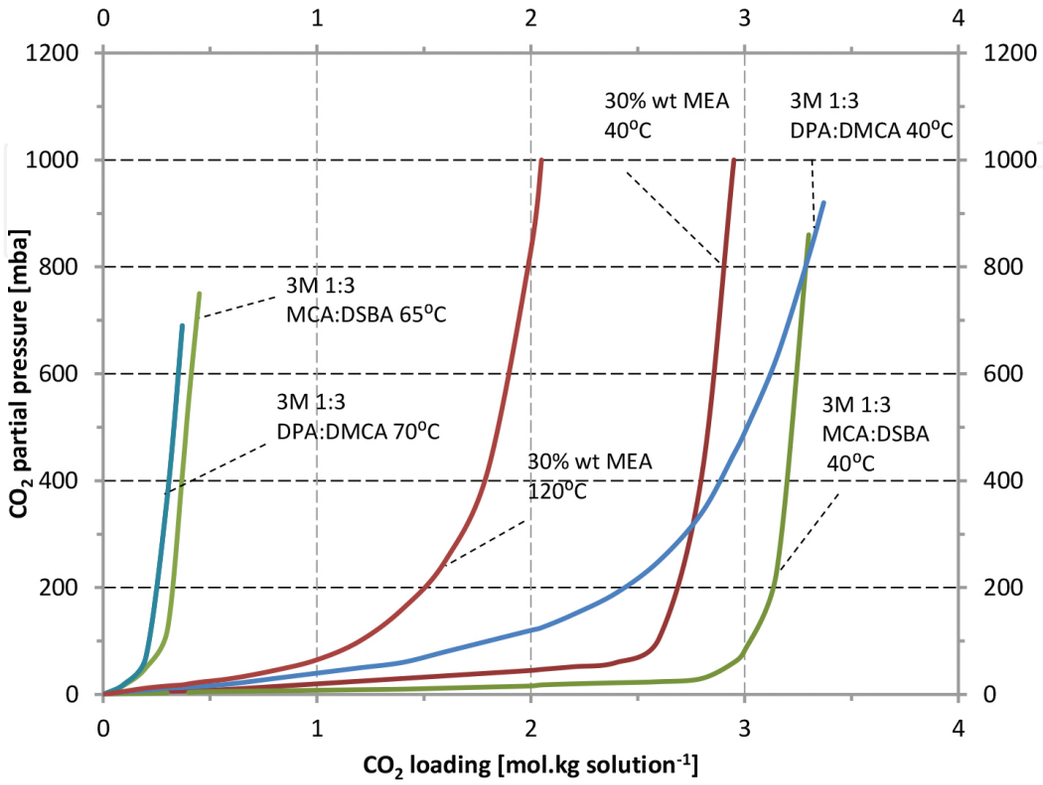


**Figure 2.** Loading curves ($CO_2$ absorption isotherms) of 3M 1:3 MCA:DSBA and DPA:DMCA at absorption and regeneration temperatures [12].

The Dortmund group also disclosed some coded proprietary biphasic absorbents [19, 20].

IFP Energies nouvelles has screened a large number of amines and identified DMX-1 [21]. DMX (implying de-mixing, i.e., phase separation) is an aqueous amine solution [22] (US 8,361,424 B2, US 8,500,865 B2, US 8,562,927 B2, US 2011/0185901 A1, WO2007/104856 A1, and US 2007/0286783 A1). After absorbing $CO_2$ at 40°C, the absorbent is heated to achieve phase separation and form a $CO_2$-rich phase and a $CO_2$-lean phase. In the subsequent regeneration process, a decanter is installed between the cross heat exchanger of lean (outlet stream from the stripper) and rich phase ($CO_2$-loaded stream from the absorber), and the regeneration is operated at 90°C under which two phases are formed. The $CO_2$-rich phase, up to 75% of the absorbed $CO_2$, obtained in the decanter is sent to the stripper and the remaining $CO_2$ is stripped in the stripper. This process could reduce the stripping burden thereby enhancing the regeneration efficiency [23].

In another report, two amine solutions (Amine B and Amine D) of a single tertiary alkanolamine with high dielectric constant have been studied [24]. The high dielectric constant of the alkanolamine is believed to trigger phase separation and to prevent solid precipitation. It has been reported that their $CO_2$ absorption loadings at 40°C and 0.1 bar are comparable to that of

MEA (**Table 2**), although the $CO_2$ loading in the $CO_2$-rich phase is not as concentrated as that with the 3H absorbents [18, 25]. Their $CO_2$ absorption isotherm is shown to be different from that of MEA (**Figure 3**) with a sharp decrease of the $CO_2$ loading in the low-pressure region, which is similar to the absorbents developed by the Dortmund's group (**Figure 2**). This feature makes it possible to achieve high cyclic loadings (e.g., 10.56–14.08 wt%). Compared to MEA technology, the use of DMX-1 could lead to 3.8% increase in power plant efficiency and 15.4% reduction in cost [26].

| | **MEA** | **Molecule D** | | **Molecule B** |
|---|---|---|---|---|
| Amine wt% | 30 | 30 | 50 | 30 |
| mol $CO_2$ per kg before flash (40°C; 0,1bar $CO_2$) | 2.6 | 2.4 | 3.2 | 2.8 |
| $CO_2$ wt% in absorbent | 11.44 | 10.56 | 14.08 | 12.32 |
| $CO_2$ % flashed | 15 | 50 | 65 | 75 |
| $CO_2$-rich phase % | | 89 | 63 | 73 |
| Flow reduction in stripper % | | 11 | 37 | 27 |

**Table 2.** IFP DMX absorbent performance (data from [24]) [9].

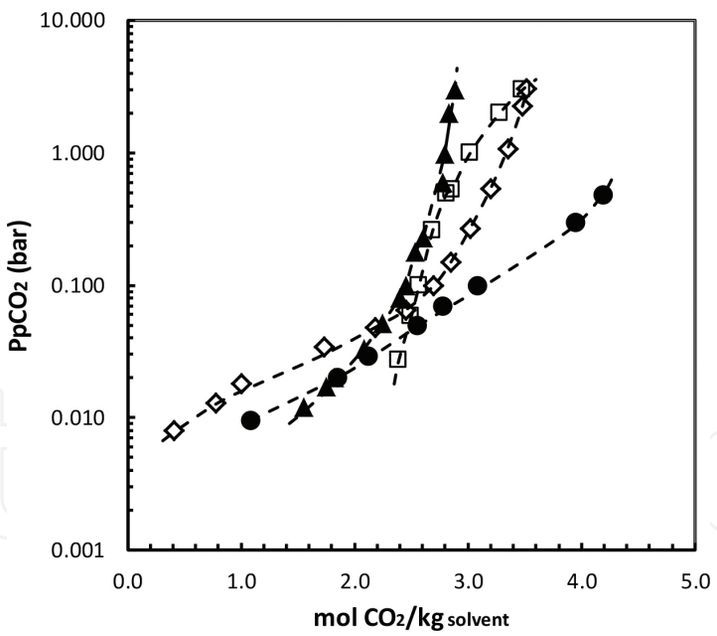


**Figure 3.** Partial pressure of $CO_2$ versus loading of a 30% wt MEA (□), a 30% wt molecule B (▲), 30% (◊) and 50% wt (●) molecule D aqueous solutions, at 40°C [24].

In another two studies, approximately 30 aqueous amines (lipophilic amines and alkanolamines) and the combination of them were screened and shown in **Table 3** (The amines appeared in **Table 1** are not included in **Table 3**) [27, 28]. Two promising examples were identified as mixtures of 2M BDA/4M DEEA (2B4D) and 2M DMBA/4M DEEA (2D4D); BDA

and DMBA are lipophilic amines, and DEEA is a tertiary alkanolamine. These two mixtures were found to have about 97% of the absorbed $CO_2$ in the lower phase along with a total loading of 0.51 mol $CO_2$/mol amine, and had a cyclic loading of 46% higher than MEA (30 wt%). Their $CO_2$ absorption isotherms were similar to those of the DMX absorbents [24] and the Dortmund's biphasic absorbents [12, 13], and their overall performance was also similar to the DMX absorbents. $^1$H NMR phase composition analysis and $CO_2$ absorption kinetics studies showed that the biphasic solvent separation was due to the fast reaction rate of BDA with $CO_2$ and the limited solubility of DEEA in the reaction products. It was concluded that the phase separation was determined by thermal dynamics of all of the species existing in the $CO_2$-loaded system, the temperature, and pressure of the $CO_2$ (**Table 4**).

| Chemical | Abbreviation | Molar mass |
|---|---|---|
| Diisopropylamine | DIPA | 101.19 |
| N-Ethyl-n-butylamine | EBA | 101.19 |
| Triethylamine | TEA | 101.19 |
| Diallylamine | DAA | 97.16 |
| Benzylamine | EMAA | 107.15 |
| N,N-Diethylethanolamine | DEEA | 117.19 |
| N-Ethylethylenediamine | EEDA | 88.15 |
| N,N-Dimethyl-1,3-propanediamine | DMPDA | 102.18 |
| 1,4-Diaminobutane | DAB or BDA | 88.15 |
| N,N-Dimethylbutylamine | DMBA | 101.19 |
| Hexylamine | HA | 101.19 |
| 1,6-Hexanediamine | HAD | 116.2 |
| N-Methyl-1,3-Diaminopropane | MAPA | 88.15 |

**Table 3.** Amines screened (data from [27, 28]) [9].

| | Phase split (wt%) | BDA (mol/kg) | DEEA (mol/kg) | $CO_2$ (wt%) | $CO_2$ (mol/mol amine) |
|---|---|---|---|---|---|
| Upper $CO_2$ lean | 22 | 0.115 | 7.265 | 0.315 | 0.026 |
| Lower $CO_2$-rich phase | 78 | 2.233 | 2.4 | 3.291 | 0.43 |

**Table 4.** Phase composition of $CO_2$-loaded 2B4D (data from [27, 28]).

An absorbent with a composition of BDA and DEEA the same as those found in the $CO_2$-rich phase was further studied. Phase separation was observed in this absorbent and the single liquid phase started to become two liquid phases at $CO_2$ loadings at 0.099 mol $CO_2$/mol amine, and from loadings of 0.187 to 0.313 mol $CO_2$/mol amine, BDA further reacted with $CO_2$ while DEEA transferred to the upper phase. Between loadings of 0.313 and 0.345 mol $CO_2$/mol, DEEA

reacted with $CO_2$ with the products transferred to lower phase until the equilibrium loading of 0.505 mol $CO_2$/mol amine was achieved [29] (**Table 5**).

| Amine or mixture of amines | Concentration | Initial $CO_2$ absorption rate (NL/min) | $CO_2$ absorption capacity (wt%) | Cyclic capacity (wt%) | Regeneration depth (%) |
|---|---|---|---|---|---|
| AMP/PZ | 3 M/1 M | 0.47 | 11.44 | 0 | 0 |
| AMP/MAPA | 3 M/1 M | 0.44 | 11.44 | 8.36 | 73.1 |
| DMMEA/PZ | 3 M/1 M | 0.44 | 10.12 | 9.24 | 91.3 |
| DMMEA/MAPA | 3 M/2 M | 0.49 | 13.2 | 7.48 | 56.7 |
| DMMEA/PZ | 5 M/2 M | 0.48 | 12.76 | 11.44 | 89.7 |
| DMMEA/MEA | 5 M/2 M | 0.44 | 10.56 | 9.68 | 91.7 |
| DMMEA/MAPA | 5 M/2 M | 0.49 | 12.76 | 9.24 | 72.4 |
| DMMEA/MAPA | 5 M/1 M | 0.47 | 14.08 | | |
| DEEA/PZ | 3 M/1 M | 0.5 | 12.32 | 0 | 0.0 |
| DEEA/MEA | 5 M/2 M | 0.44 | 6.6 | 0 | 0.0 |
| TRIZMA/PZ | 3 M/1 M | 0.44 | 7.92 | 7.04 | 88.9 |
| TRIZMA/MEA | 3 M/1 M | 0.33 | 4.4 | 3.96 | 90.0 |
| TRIZMA/MAPA | 3 M/1 M | 0.43 | 8.36 | 5.28 | 63.2 |
| MEA | 5 M | 0.48 | 11.44 | 4.84 | 42.3 |
| MAPA | 5 M | 0.5 | 19.36 | 4.84 | 25.0 |

Data in the table were read from the graphs in [30]. This operation may introduce an uncertainty of ±5–10%.

**Table 5.** $CO_2$ Absorption and regeneration of aqueous amine or binary amine systems.

To identify absorbents with low regeneration energy, researchers from the Norwegian University of Science and Technology screened multiple aqueous amines or mixture of amines [30]. They found that DMMEA/PZ (3M/1M, 5M/2M), especially 3M/1M, and DMMEA/MEA (5M/2M), had high $CO_2$ absorption rate and characteristics of deep regeneration at low temperature, almost doubling the cyclic loading of the MEA. Further, these researchers developed biphasic absorbents of DEEA/MAPA, tertiary alkanolamine and lipophilic amine [31, 32]. They examined the vapor liquid equilibrium (VLE) of $CO_2$-DEEA-MAPA-$H_2O$ system at 40, 60, and 80°C, from which the $CO_2$ absorption loading, absorption phase split ratio, and phase compositions were derived as presented in **Table 6**. The absorbed $CO_2$ was found to be highly concentrated in the $CO_2$-rich phase, which alone was shown to have a much deeper regeneration hence a higher cyclic loading compared to aqueous MEA (**Figure 4** (Figure 17 in [31]). However, the $CO_2$-DEEA-MAPA-$H_2O$ system had a higher viscosity compared to MEA and its $CO_2$ absorption kinetics was faster but dropped down slower with increasing $CO_2$ loading. In their pilot plant trials at a scale of 80–90 $m^3$/h flue gas with $CO_2$-rich/$CO_2$-lean phase

separation and $CO_2$-rich phase regeneration, their system was shown to be superior to aqueous MEA, which was tested in the pilot plant as well [33, 34]. This finding was supported by modeling the biphasic absorbent with an energy consumption of 2.2-2.4GJ/t$CO_2$ and compared to 3.7GL/t$CO_2$ using 30wt% aqueous MEA [32, 35].

| **Temperature (°C)** | **40** | **60** | **80** |
|---|---|---|---|
| $CO_2$ pressure (kPa) | 13.07 | 13.07 | 13.07 |
| $CO_2$-rich phase fraction | 0.68 | 0.53 | 0.48 |
| $CO_2$ loading mol/kg (mol/kg) and in (wt%), total | 2.86 | 2.43 | 2.11 |
| | 12.58 | 10.69 | 9.28 |
| $CO_2$-rich phase loading (mol/L) and in (wt%) | 5.55 | 5.66 | 5.44 |
| | 24.42 | 24.90 | 23.94 |
| $CO_2$ lean phase loading (mol/L) | 0.28 | 0.29 | 0.1 |

**Table 6.** Phase compositions of DEEA/MAPA (5M/2M) [31, 32].

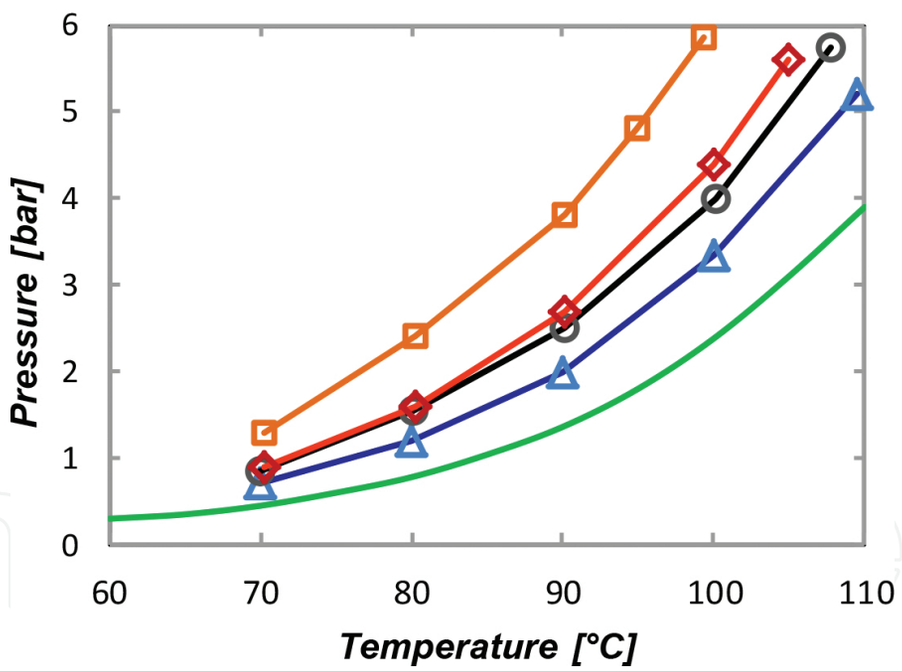


**Figure 4.** The total pressure from lower phase samples with absorption taken at 40°C from the screening apparatus. $P_{CO2}$: (Δ) 6 kPa, (O) 8 kPa, (◊) 10 kPa, and (□) 13 kPa; (green line) MEA at loading 0.5 mol $CO_2$/mol MEA (model from [36]) [31].

In summary, up to now, researchers and developers have achieved encouraging results in the area of liquid-liquid biphasic $CO_2$ absorbents, and some biphasic absorbents can be regenerated at lower temperatures with deeper regenerability than the bench mark aqueous MEA (**Table 7**).

| Developer | Biphasic absorbent | Phase separation temperature | Regeneration temperature | Regeneration depth | Source |
|---|---|---|---|---|---|
| 3H Company | Nonaqueous, alkanolamine/alcohol | Absorption temperature, 40°C | Up to 125°C | 90% | [18, 25] |
| Korean Institute of Energy Research | Non-aqueous, MEA in 1-heptanol, isooctanol, 1-octanol | Absorption temperature | N/A | N/A | [17] |
| Dortmund University | MCA/DSBA; DPA/DMCA; DMCA/MCA/AMP | 60–70°C | Up to 75°C | 90+% | [12, 13] |
| IFP Energies nouvelles | DMX-1; Amine B; Amine D | 90°C | >90°C | 90+% | [24] |
| Tsinghua University | DEEA/BDA | 40°C | 90°C | 90% | [27, 28] |
| Norwegian University of S&T | DEEM/MAPA | 80°C | >80°C | ~90% | [31, 34, 35] |

**Table 7.** Summary of the developed biphasic absorbents for $CO_2$ capture.

## 3. Liquid-solid biphasic absorbent systems

There is a category of liquid absorbents forming solid precipitates after $CO_2$ absorption such as carbamate, bicarbonate, or carbonate in solid states. According to Le Chatelier's Principle [37], formation of a solid product during $CO_2$ absorption and its removal from the solution phase shifts the reaction equilibrium toward the production of more products. This phenomenon could be engineered and developed to potentially more efficient carbon capture technology.

### 3.1. Emulsion of alkanolamine and ionic liquid (IL)

Research has been going on to use ILs as absorbents for $CO_2$ capture because ILs have negligible volatility, nonflammability, high thermal stability, and virtually unlimited chemical tunability. However, stand-alone, ILs are not competitive enough when compared to $CO_2$ capture efficiency of aqueous alkanolamine systems. An idea is to try hybrid system coupling advantages of alkanolamines with those of room-temperature ILs (RTILs) and to achieve potential synergies arising from each of the individual components [38].

A mixture of diethanolamine (DEA) and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, which is hydrophobic, was tested for $CO_2$ absorption (**Figure 5**). This emulsion could capture $CO_2$ up to the stoichiometric maximum through crystalizing $CO_2$-bonding product (DEA-carbamate) while avoiding equilibrium limitations and thus making efficient utilization of the absorbent molecules [39]. Similar precipitation of carbamate

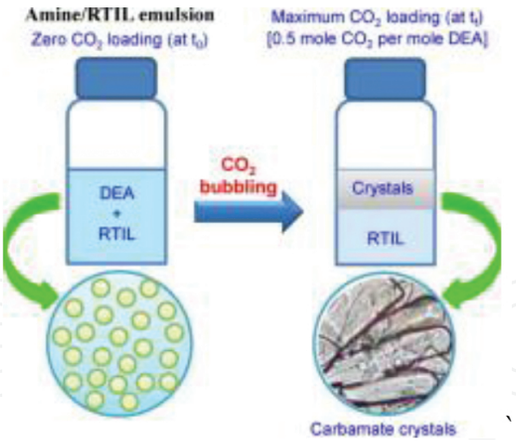


**Figure 5.** Immiscible alkanolamine/RTIL system for efficient $CO_2$ captures [39].

upon $CO_2$ absorption was also observed with ILs such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][$Tf_2N$]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][$Tf_2N$]), and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([HMIM][$Tf_2N$]). The density of the solid phase precipitates was lighter thereby quickly rising to the surface and easing the separation for regeneration (**Figure 6a–c**). Hydrophobicity of ILs plays a role in the separation of solid products from

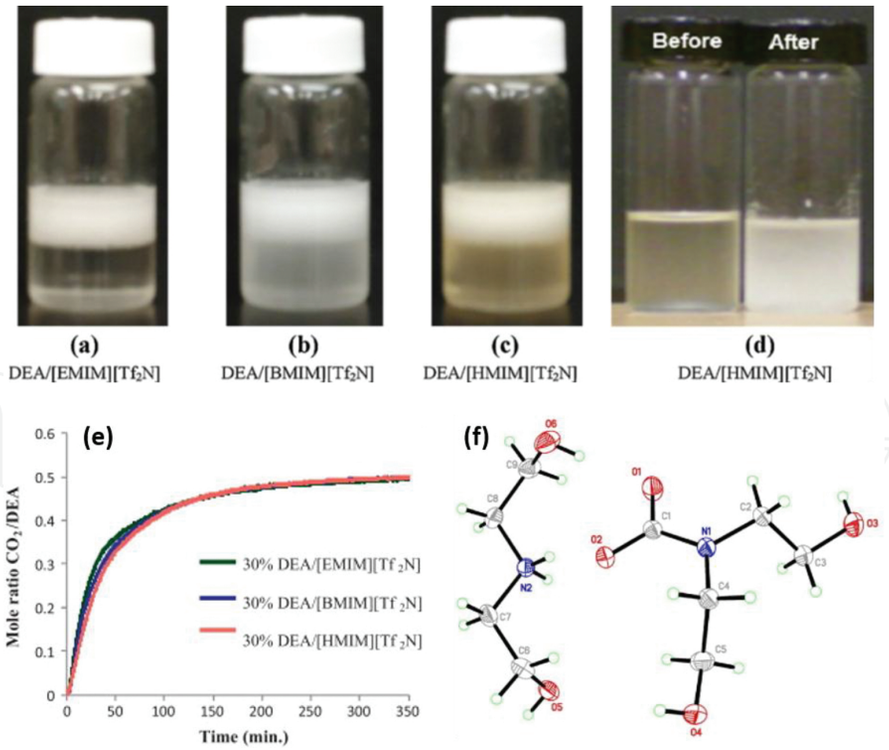


**Figure 6.** DEA/RTIL system for $CO_2$ capture: (a–c) (without surfactant) after $CO_2$ capture; (d) (with surfactant) before and after $CO_2$ capture; (e) $CO_2$ capture capacity profiles of the DEA/RTIL system at atmospheric pressure and 25°C; and (f) basic structural unit in DEA-carbamate ($C_9H_{22}N_2O_6$) crystal [39].

the liquid phase. When a surfactant, Triton® X-100, was added to the [HMIM][$Tf_2N$]-based system, the carbamate product remained dispersed in the suspension (**Figure 6d**). $CO_2$ loading capacity up to the stoichiometric maximum (0.5 mole of $CO_2$ per mole of DEA) can be achieved. The three absorbents showed similar $CO_2$ uptake rates (**Figure 6e**). The crystallization of the carbamate product, which was composed of protonated-DEA cation and DEA-carbamate anion (**Figure 6f**), enabled higher $CO_2$ uptake, and solid precipitation may have facilitated the separation thereby offering advantages in regenerating a smaller (only solid carbamate) volume with less energy consumption.

Other systems of aqueous solutions of N-methyldiethanolamine (MDEA) and guanidinium tris(pentafluoroethyl) trifluorophosphate $[gua]^+[FAP]^-$ IL showed similar solid formation after the absorption of $CO_2$ at high pressures. The formed $CO_2$-bonding solid products could be easily regenerated (**Figure 7**) [40].

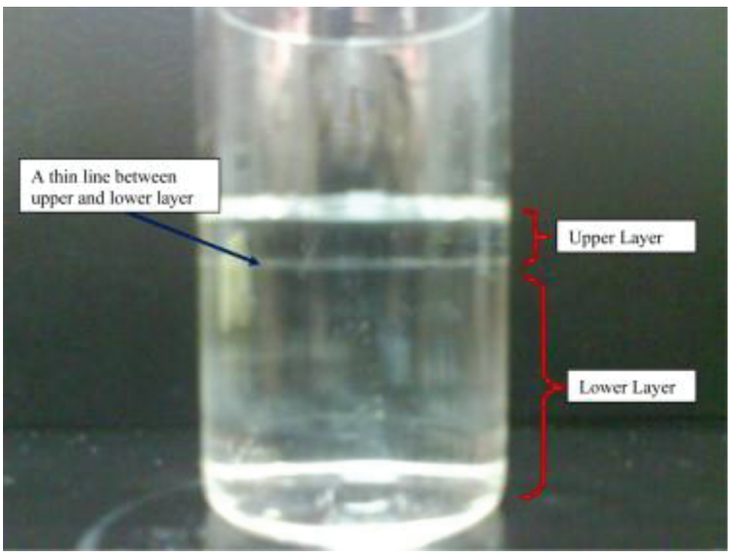


**Figure 7.** A photo of double layer $CO_2$-rich mixtures [40].

### 3.2. Chilled ammonia

Aqueous ammonia can absorb $CO_2$ to produce solid ammonium carbamate/bicarbonate, which could be separated from the solution thereby allowing an efficient recycling of the unreacted scrubbing solution [31, 41, 42]. Chilled ammonia process could be developed using aqueous ammonia to absorb $CO_2$ at lower temperature (2–10°C), in which the ammonia slip from the absorber could be reduced and the flue gas volume could be smaller [43].

Precipitation of pheromone in ethanol-water chilled ammonia solution was also observed after $CO_2$ absorption [44]. In this $CO_2$ absorption process, solid mixtures of ammonium bicarbonate and ammonium carbamate, or of ammonium carbamate alone were formed. Selective formation or precipitation of solid ammonium carbamate could be obtained by reacting gaseous $CO_2$ and $NH_3$ in anhydrous ethanol, 1-propanol, and N,N-dimethylformamide (DMF) in a flow reactor that can operate continuously. After filtering the solid precipi-

tates, the unreacted ammonia solution could be reclaimed into the absorber. Such a chilled ammonia process may be applied to capture $CO_2$ from flue gas of coal-fired boilers, natural gas combined cycle systems, and other energy heavy industrial applications [45].

### 3.3. Triethylenetetramine (TETA)/ethanol solution as absorbent

When $CO_2$ is absorbed into a solution of triethylenetetramine (TETA) dissolved in ethanol, solid precipitates formed (**Figure 8a** and **b**) in contrast to TETA/water solution [46]. Moreover, TETA/ethanol solution showed improvement in $CO_2$ absorption rate, absorption capacity, and absorbent regenerability. Ethanol not only promoted the solubility of $CO_2$ in the liquid phase but also facilitated the chemical reaction between TETA and $CO_2$. The $CO_2$ capacity of the solid phase as TETA-carbamate accounted for about 81.8% of the total $CO_2$ absorbed (**Figure 8c**). The TETA/ethanol solution was found to be relatively stable throughout multiabsorption-desorption cycles (**Figure 8d**). One hurdle of applying the TETA/ethanol solution for $CO_2$ removal is that ethanol has a high vapor pressure and this must be taken into consideration for further development of this absorbent system and later designing for possible commercial applications.

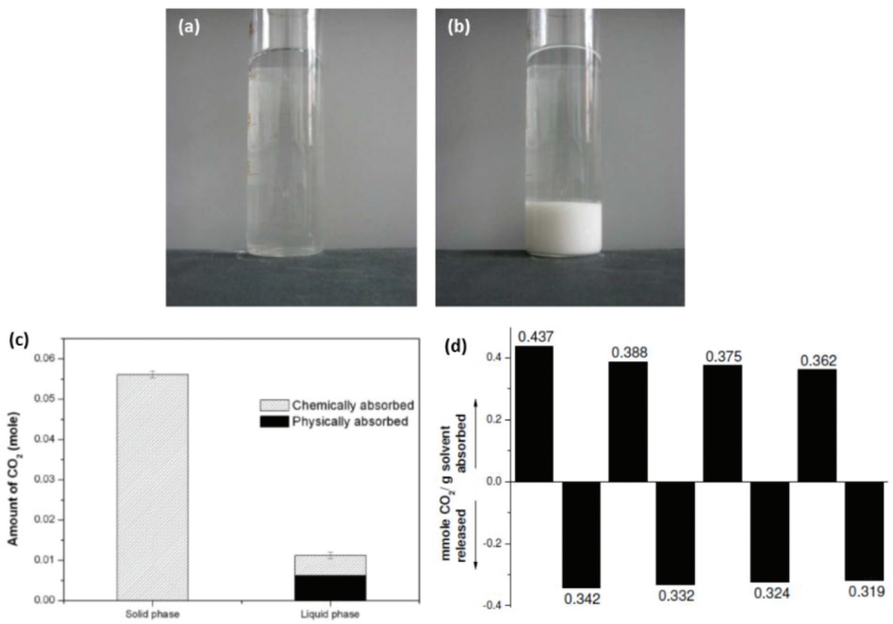


**Figure 8.** TETA/ethanol solution (a) before $CO_2$ absorption and (b) after $CO_2$ absorption. (c) Partition of carbon dioxide in the solid phase and liquid phase. (d) Cycling absorption/regeneration runs of TETA/ethanol solution for $CO_2$ absorption [46].

### 3.4. Amino acid salt as liquid-solid phase change absorbent

Being environmental friendly, ionic nature and low volatile, amino acid salts are of great interest as potential solvents for $CO_2$ capture [47, 48, 49]. Moreover, amino acid salt solutions have good resistance to an oxygen-rich flue gas stream. The reactivity of amino acid salts with $CO_2$ is similar to those of alkanolamines due to the presence of identical amino functional

groups in their molecules. Some of them such as the potassium salts of glycine, sarcosine, and proline, react faster with $CO_2$ than MEA thereby kinetically favorable [50, 51].

Multiple amino-acid salts were found to precipitate after reacting with $CO_2$ to a certain degree [52]. During the absorption of $CO_2$ in aqueous potassium salts of N-methylalanine, DL-alanine, and $\alpha$-aminoisobutyric acid, solid precipitates were observed [53]. Various types of solid precipitates could be achieved by varying the amino acid structure and solubility. Amino acids with a primary amino group may form only zwitterion species precipitates [54], while amino acids with a hindered amino group and with relatively high zwitterion solubility (e.g., proline) may form potassium bicarbonate precipitates [55].

By Le Chatelier's Principle, the driving force for $CO_2$ absorption can be maintained at a high level even at high loadings. Thus the absorber performance could be significantly improved. This effect was indicated in **Figure 9** (enhanced absorption) where the possible precipitates were highlighted. In **Figure 9**, besides the heat input necessary to regenerate the solvent, in the case of precipitating amino acids two more effects are possible: Enhanced absorption (purple) due to the precipitation of reaction products during absorption and enhanced

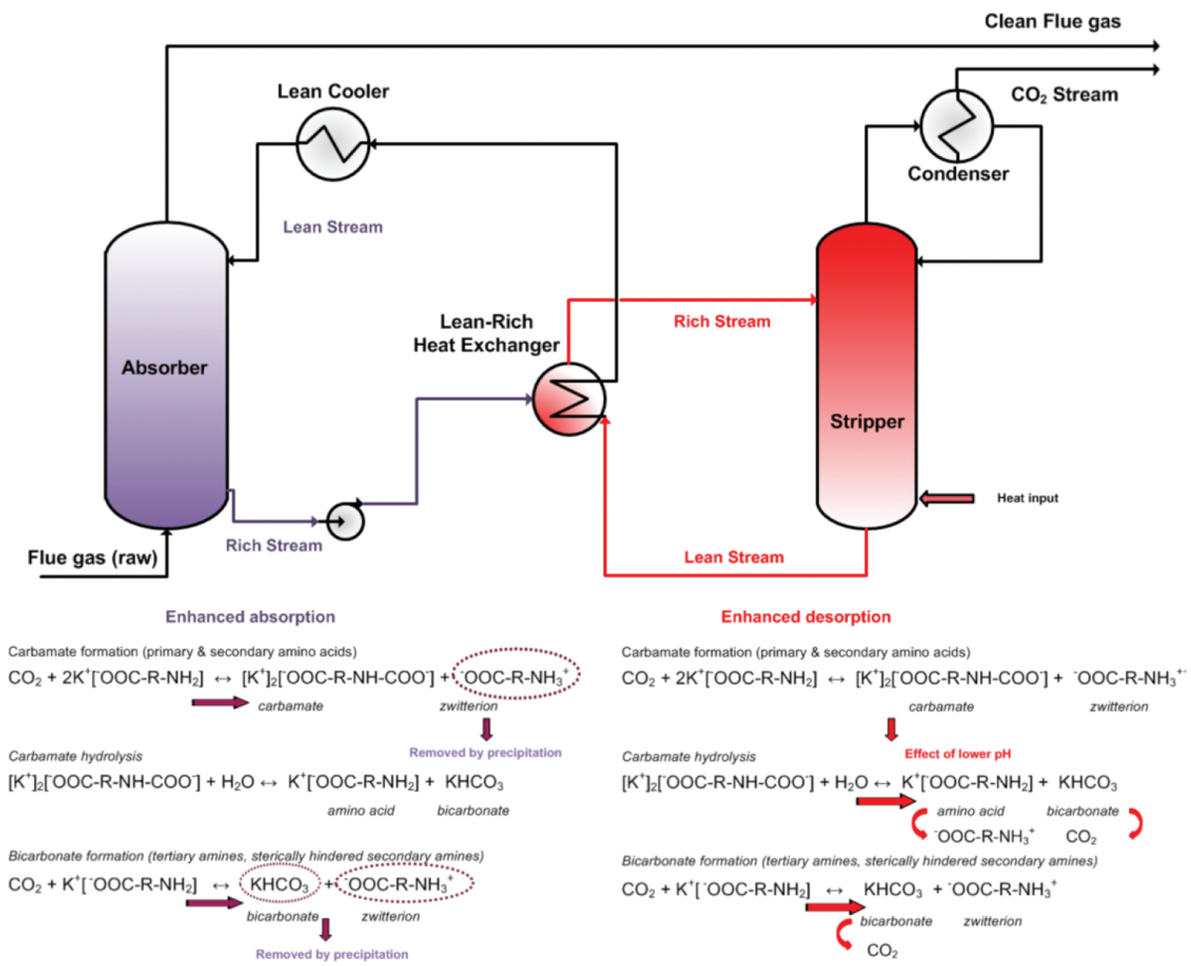


**Figure 9.** Conventional amine-based process for $CO_2$ capture where the reactions specific to amino acid salts have been added at the bottom of the absorber and the stripper [56].

desorption (red) due to a lower pH that results from increasing the amino acid to $K^+$ ratio in solution [56]. Because of the high loadings, the regeneration energy consumption was reduced [57]. As can be seen from **Figure 10**, at a given $CO_2$ partial pressure, a precipitating-based process would have higher loading than a conventional absorption process without precipitation, and a combined process (simultaneous absorption and precipitating process) is expected to result in increased capacity.

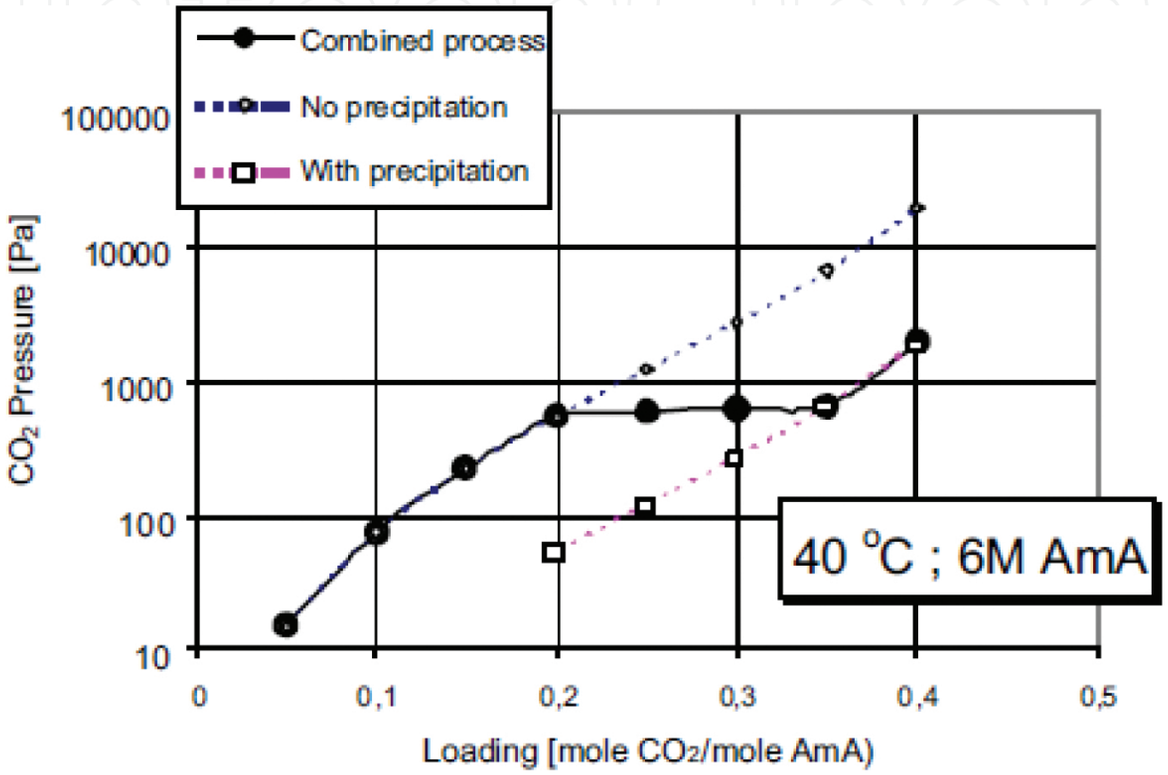


**Figure 10.** Schematic picture to depict the difference between a precipitating and a nonprecipitating system in terms of $CO_2$ pressure as a function of loading [58].

**Figure 11** shows a schematic representation of the DECAB process for liquid-solid phase change amino acid salt absorbent [56]. The flue gas (at 40°C) is contacted with $CO_2$ preloaded absorbent in a spray-tower, resulting in that the $CO_2$ undergoes a chemical reaction with the absorbent that leads to the formation of carbamate and carbonate ions, as shown in **Figure 11**. As absorption goes on, the pH of the absorbent solution as well as solubility of the amino acid decreases. Finally, the $CO_2$-bonding amino-acid precipitates as an amino acid zwitterion. In the process, the solid precipitates are collected at the bottom of the tower. The remaining $CO_2$ in the flue gas is captured in the absorption column, where the depleted flue gas is contacted with lean absorbent. The absorption column is a conventional packed absorption column filled with structured packing. There, the $CO_2$ partial pressure is reduced to the desired value for 90% $CO_2$ removal. The rich stream containing the solids, is further processed in the stripper, via the lean-rich heat exchanger, to release the $CO_2$. The lean-rich heat exchanger also needs to be able to handle solids (e.g., spiral heat exchanger).

The $CO_2$ absorption depth needs to be controlled so that only in the spray-tower the solid products are formed [56].

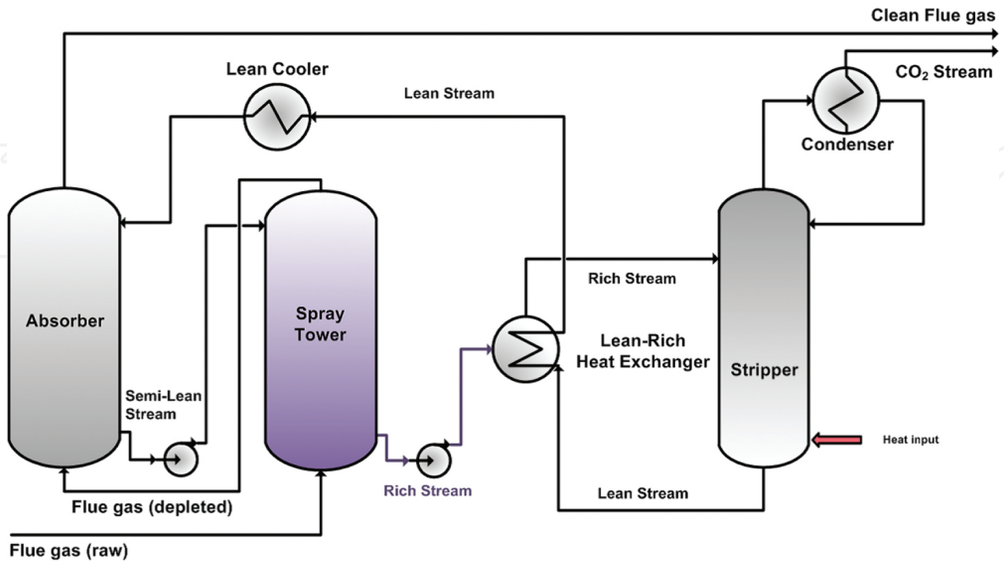


**Figure 11.** DECAB process concept for $CO_2$ capture. Enhanced absorption due to the precipitation of reaction products during absorption is highlighted in purple [56].

## 4. Enzymatically catalyzed absorbent systems

A special enzyme, carbonic anhydrase (CA), works in vertebrates' lungs to facilitate oxygen and $CO_2$ exchange through respiration in a very fast and effective way. Attempts to incorporate this type of enzyme to carbon capture absorbent systems have shown encouraging results [59]. When a small quantity of the enzyme is used as catalyst in a $CO_2$ capture absorbent system (usually an aqueous amine absorbent), it enhances the reaction rate and enables rapid approach to equilibrium between dissolved $CO_2$ and $HCO_3^-$ in aqueous solutions. The idea is a natural extension of the experience that some enzymes have been successfully deployed to increase the efficiency of other industrial processes [60, 61]. The enhancement effect of the enzyme is so significant that the size of an absorber could be reduced up to 90% smaller than the conventional amine case [61]. However, enzymes are bio active compounds. How to maintain its long period activity is an issue. The Canadian company, *$CO_2$ Solutions*, reported that their developed enzymatic catalytic amine system could work for 15 days for $CO_2$ capture in temperature ranges of 40–70°C [61].

The way to implement enzyme more effectively in $CO_2$ capture process is to support or immobilize it onto some sort of carrier to provide sustained stability under working conditions. It may need to be able to stand for the high regeneration temperature if the enzyme is not confined in the absorber only. Report shows that some developed enzyme systems could stand for moderate regeneration temperatures (e.g., around 70–80°C) [59]. The immobilized enzyme should also be strong toward contaminants encountered in the common flue gas.

A porous organosilica coating containing CA to separate $CO_2$ from a flowing gas stream has been tested [62]. This coating was applied to ceramic random packing and placed in a counter-current absorber column, where it demonstrated a high rate enhancement for 400 days at 45°C and a total turnover number of ~48 million moles $CO_2$/mole enzyme. In another development, the same coating formulation was deposited onto stainless steel structured packing. This coating technique was used to produce 275 liters of packing for pilot testing at the National Carbon Capture Center in Wilsonville, AL, on coal-fired flue gas. This unit operated for nearly 5 months at 40°C in the same carbonate solution and exhibited a steady 80% $CO_2$ capture.

A type of magnetic polymer microspheres functionalized with epoxy group was prepared, and CA enzyme was immobilized on the carriers by selectively covalent binding [63]. The parameters affecting CA immobilization, such as pH, temperature, and enzyme dose were investigated. The kinetic parameters of the immobilized and the free CA were also evaluated. The value of the Michaelis–Menten constant ($K_m$) and the maximum velocity ($V_{max}$) of the immobilized CA were 8.077 mmol/L (mM) and 0.027 μmol/(min mL), respectively, while those of the free CA were 6.091 mM and 0.091 μmol/(min mL), respectively. Moreover, the performance of the thermal stability, storage stability, and reusability of the immobilized CA confirmed that CA immobilized on the epoxy-functionalized magnetic polymer microspheres possessed a stable and efficient catalytic ability on $CO_2$ hydration, which seemed to be a suitable candidate for $CO_2$ capture [63].

In another development, new materials of $Fe_3O_4$ magnetic microspheres were functionalized with carboxyl groups and prepared for CA immobilization to capture $CO_2$. The optimum conditions for immobilization, such as carrier dose, enzyme dose, pH, shaking speed, temperature, and contact time, were examined. The pH and thermal stability of the free and the immobilized CA were compared. The results showed that the immobilized CA had a better enzyme activity, a higher pH and thermal stability than those of free CA. Meanwhile, $CO_2$ capture was significantly enhanced by the free and immobilized CA in tris(hydroxymethyl) aminomethane (Tris) buffer solution. Moreover, the immobilized CA maintained 58.5% of its initial catalytic activity after 10 recovery cycles due to the protection effect of the magnetic microspheres. All the results confirmed the potential merits of using the carboxyl-functionalized $Fe_3O_4$ magnetic microspheres immobilized CA to remove $CO_2$ from air or flue gas [64].

## 5. Encapsulated absorbents

Many attractive options for carbon capture solvents suffer from high viscosity, making it difficult to generate large surface areas for fast absorption, and amine-based aqueous liquids suffer from potential environmental impacts from ammonia (product of amine decomposition), and amine vapor release. Microencapsulated carbon sorbents (MECSs) are a new class of carbon capture materials consisting of a $CO_2$-absorbing liquid absorbent contained or confined within solid, $CO_2$-permeable polymer shells. As part of a US-DOE ARPA-E program, a team from the University of Illinois Urbana-Champaign, Babcock and Wilcox, and the Lawrence Livermore National Laboratory has created this new type of encapsulated form of

carbon capture absorbent in which the operating fluid, amines, or carbonates in the tests are enclosed in a thin polymer shell forming 200–400 μm beads [65]. While mass transport across the polymer shell is reduced compared to the bulk liquid, the large surface area of the beads improves overall mass transfer more than off-setting this disadvantage. The liquid, as well as any degradation products or precipitates, remain encapsulated within the beads, which can be thermally regenerated repeatedly. Encapsulated absorbents have the capacity of the liquid absorbents as well as the physical behavior of solid sorbents. It could be imagined for them to be useful in fairly conventional-style capture applications, as well as unprecedentedly new approaches facilitated by their high surface area. The developed beads appear to be both chemically and mechanically stable under typical industrial conditions. There are engineering constraints that the beads must satisfy for several application strategies, including their use in fluidized beds and these should be further studied. The US group has encapsulated MEA, piperazine, and a variety of other carbonate solutions, which appear to be optimal for this application, demonstrating rapid $CO_2$ uptake and desorption using colorimetric methods, which permit rapid spectroscopic determination of the extent of $CO_2$ uptake and release. Carbonate capsules are created using a silicone polymer shell which is both rugged and permeable to $CO_2$. Results of mechanical/thermal cycling tests demonstrate long-term stability of silicone-encapsulated carbonate [65].

Especially, MECS enhances the rate of $CO_2$ absorption for solvents with slow kinetics and prevent solid precipitates from scaling and fouling equipment, two factors that have previously limited the use of sodium carbonate solution for carbon capture. Researchers have examined the thermodynamics of sodium carbonate slurries for carbon capture [66]. Modeling work has been carried out on the vapor-liquid-solid equilibria of sodium carbonate and several features that can contribute to an energy-efficient capture process have been derived: very high $CO_2$ pressures in stripping conditions, relatively low water vapor pressures in stripping conditions, and good swing capacity. These would make a more effective and efficient $CO_2$ absorption and desorption cycle. The high potential energy savings have been indicated compared with an MEA system [66].

## 6. Direction for further development

### 6.1. Liquid-liquid biphasic absorbent

The following aspects are recommended for future studies:

- As to liquid-liquid biphasic absorbent systems that have already been identified, detailed, and comprehensive $CO_2$ absorption and kinetics studies are much needed. Continuous mass transfer from $CO_2$-lean phase to $CO_2$-rich phase, diffusion of multispecies within the absorbent, and viscosity should be considered as $CO_2$ absorption continues. Based on knowledge obtained from these current amines studied, screening, designing, and synthesizing of new amines with improved properties are possible.

- For regeneration, $CO_2$ taken from the exit of the regenerator may be used as heat-transferring and stripping gas, and a heat exchanging unit may be installed in the stripper/regenerator. It is also possible to increase the regeneration pressure so that the size of the regenerator can be reduced hence reducing capital cost and energy consumption; some biphasic absorbents have high equilibrium $CO_2$ pressures.
- Phase separation temperature should be optimized to reduce energy consumption during regeneration; phase separation temperatures close to absorption temperature may be preferred. Feasibility studies including modeling and economic evaluation should be conducted to obtain overall performance, absorber/regenerator sizing, energy penalty, and cost of a biphasic absorbent carbon capture plant. In addition, pilot plant demonstrations of promising biphasic absorbents need to be considered.

### 6.2. Other emerging absorbents

For liquid-solid phase change absorbents, one of the biggest challenges related to their applications is to have a process design that could handle solids/precipitates transportation, heat exchanging, and regeneration. Process designs like the ones (i.e., DECAB process, DECAB Plus process) proposed for liquid-solid phase change amino acid salt absorbent could be adapted for other liquid-solid phase change systems as well [58].

Enzymes are macromolecular proteins and their current research has been focusing on their effects on $CO_2$ capture performance. The aspects of their active life span, the process of mass production or extraction from natural sources, and the related costs should be further explored.

For the encapsulated absorbents, within capsule kinetics and overall mass transfer studies should be pursued. The technology of mass production and the costs are also key factors in determining its commercial viability for $CO_2$ capture application. Techno-economic feasibility studies are keenly welcome.

In summary, most of these technologies are still at laboratory research stage, and there remain challenges associated with the scale-up of these technologies to meet the needs of $CO_2$ capture from power generation as well as other energy heavy industries. Future efforts should be focused on developing basic theoretical and mechanistic understandings of phase change, mass transfer, and $CO_2$ absorption and desorption phenomena, to perform pilot plant testing to generate design parameters and process requirements, and to create in parallel techno-economic plant design fundamentals and packages for proving the feasibilities of these emerging carbon capture absorbents.

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