

Phase-Change Solvents for CO₂ Capture

Xianfeng Wang, Bingyun Li

Department of Orthopaedics, West Virginia University, Morgantown, WV, USA

1. Introduction

With the rapid increase of the global population and the industrialization of more and more countries, the consumption of energy is growing explosively. Currently, over 85% of the global energy demand is being supported by the burning of fossil fuels, which releases large amounts of carbon dioxide (CO₂) into the atmosphere.^{1,2} As a result, CO₂ concentration in the atmosphere has increased since the beginning of industrialization at an accelerating rate to ~390 ppm in 2010.^{3,4} The increase of CO₂ concentration in the atmosphere and fears of resulting catastrophic global climate change have led to increased demand for CO₂ capture and storage (CCS) technologies.⁵⁻⁸ CO₂ absorption using chemical reaction is a common process in the chemical industry and, along with other processes, has been applied in the treatment of industrial gas streams containing acid gases like H₂S, NO_x, and CO₂. In these gas-treating processes, aqueous amine solutions are most commonly used, especially monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), and their mixtures. In principle, these systems could be used for the removal of CO₂ from flue gases, such as from power plants in a regenerative absorption–desorption process.⁹ However, these solvents have a limited cyclic CO₂-loading capacity, may lead to high equipment corrosion, require high-energy consumption for regeneration, and suffer from solvent losses by evaporation and/or degradation in an oxygen-rich atmosphere.^{10,12}

To identify cost-effective approaches for CO₂ capture, many new materials and techniques have been developed and evaluated.^{1,9,13-15} A new class of solvents, phase-change solvents, has emerged and been developed into one of the most promising technologies for CO₂ capture. Several experimental studies with absorbents that exhibit phase-change features during the absorption or desorption of CO₂ have shown promise.¹⁶⁻¹⁸ Such phase-change technology removes CO₂ from power-plant flue gases using a solvent that, when it reacts with CO₂, rapidly forms two distinct phases: a CO₂-rich phase and a CO₂-lean phase. Only the CO₂-rich phase will then undergo regeneration to remove the CO₂ and recycle the solvent. By regenerating only the CO₂-rich phase, significantly less

energy may be needed for regeneration.^{19,20} In this chapter, we will provide a comprehensive review of the state-of-the-art research activities related to phase-change solvents, including solvent design and characterization, and CO₂ capture performance and process design.

2. Conventional Chemical Absorption

Amine scrubbing has been applied to separate CO₂ from natural gas and hydrogen since 1930.²¹ A typical amine developed for this purpose is MEA. The process involves the passage of an aqueous amine solution (typically 30 wt.%) down the top of an absorption tower, while a gaseous stream of flue gas containing CO₂ is introduced at the bottom. A blower is required to pump the gas through the absorber. At a temperature of approximately 40 °C, the reaction of CO₂ with the amine occurs through a zwitterion mechanism to form carbamates.¹ The amine is regenerated by stripping with water vapor at 100–120 °C, and the water is condensed from the stripper vapor, leaving concentrated CO₂ that can be compressed to 100–150 bars for geologic sequestration. Although aqueous amine solutions are effective in removing CO₂ from natural gas under a variety of conditions, aqueous amine processes often suffer from issues with corrosion, amine oxidative degradation, and solvent losses. Additionally, the use of aqueous amine processes is highly energy intensive, largely because of the thermodynamic properties of water.²² In fact, it is estimated that almost 30% of the energy of the power plant would have to be diverted to run the CO₂ capture process, which could result in a doubling of the cost of electricity. Improved strategies for CO₂ capture include the use of liquids with lower heat of absorption and increasing the concentration of the absorbent molecules. Other compounds that are often considered are sterically hindered compounds such as 2-amino-2-methyl-1-propanol (AMP), secondary amines such as DEA, and tertiary amines such as MDEA.²³ Inorganic solvents such as aqueous potassium and sodium carbonate as well as aqueous ammonia solutions have also been considered for chemical absorption. Note that CO₂ capture from ambient air using chemical absorption in aqueous alkali hydroxide solutions has also been proposed.²⁴ Despite the strongly absorbing nature of the solutions, the large energy demands of the regeneration step present a significant challenge in postcombustion CO₂ capture from power plants.¹

3. New Solvents for CO₂ Capture

Numerous technology options exist for postcombustion CO₂ capture that are generally compatible with CCS activity. These include solid sorbents, membranes, and new liquid absorbents, as well as processes to directly convert CO₂ into carbonates or other manageable species. Solid sorbents like metal organic frameworks represent one type of new materials. However, any industrial process using solid sorbents would likely involve

temperature swing. Unfortunately, heat transfer to and from a solid support is challenging. Membranes are attractive, but scaling up to power-plant sizes would be challenging.^{25,26} Given these considerations, new liquid absorbents, representing the best alternative to aqueous amine technology, are increasingly attracting remarkable interests.

Among the emerging solvent technologies for CO₂ capture, ionic liquids (ILs) have garnered much attention and are regarded as potential candidates. ILs are commonly defined as liquids, which are composed entirely of ions with a melting point of less than 100 °C. Much of this interest is centered on the possible use of ILs as “green” alternatives to volatile organic solvents. One of the promising advantages of ILs for CO₂ capture is their negligible vapor pressure and negligible losses. The lower vapor pressure of ILs may lead to lower energy consumption during CO₂ stripping and solvent regeneration.¹ In addition to their extremely low vapor pressures, they are nonflammable, environmentally benign, and exhibit exceptional thermal stability. Moreover, numerous combinations of cations and anions can be used to produce new ILs, and this flexibility can be used to tune their chemical and physical properties for CO₂ capture.²³

Perry and coworkers have employed the concept of combining both physisorbing and chemisorbing components in one molecule to produce an aminosilicone solvent mix for CO₂ capture.²⁷ The physical-absorbing portion of the molecule would reside in the backbone and covalent CO₂ capture would sit on the termini of tethering groups. They use siloxanes, ethers, perfluoroethers, and amides as physical-absorbing species. Styrene and alkyl derivatives are also considered, based mainly on their cost and availability. Aminoethyl, aminopropyl, aminoethylaminopropyl, and other amine groups are chosen as chemically reactive functional groups. CO₂ capacity is related to the number of reactive primary and secondary amines present in the structure. To maintain a liquid state, a hydroxyether cosolvent is employed that allows enhanced physisorption of CO₂ in the solvent mixture. Regeneration of the capture solvent system is demonstrated over six cycles and absorption isotherms indicate a 25–50% increase in CO₂ capacity over 30 wt.% MEA. In addition, proof of concept for continuous CO₂ absorption is verified. Further exploration of this system is in progress with thermal stability and corrosion studies underway as well as further optimization of the amino silicone substrates.

4. Phase Change Solvents for CO₂ Capture

In the past two decades, a new class of solvents, phase-change solvents, has emerged and been developed into one of the most promising technologies for CO₂ capture. Upon CO₂ absorption, phase-change absorbents will typically form two phases with one lean in CO₂ and one rich in CO₂, which can be separated based on differences in density. The CO₂-lean phase can be recycled back to the absorber and the CO₂-rich phase can be sent to the stripper for regeneration.¹⁹ In some cases, formation of a solid phase due to

precipitation during absorption of CO₂ with aqueous solutions can be found in systems such as alkanolamine/ILs, chilled ammonia, triethylenetetramine (TETA)/ethanol solution, and amino acid salts. In this section, we will introduce recent research activities in the development of phase-change solvents, including two liquid phases and liquid–solid phases, for CO₂ capture.

4.1 Phase Change Mixed Amine Solvents

To develop cost-effective CO₂ capture processes, some research groups have focused on the reduction of regeneration energy by suggesting mixture solvent systems such as mixed amine systems. Bruder and Svendsen have found that certain blends of 2-(Diethylamino) ethanol (DEEA)/3-(Methylamino)propylamine (MAPA) can form two phases after CO₂ absorption, and the cyclic loading can be significantly higher than that of MEA.²⁸ This process is under development in the European Union project iCap.²⁹ The chemical structures of the amines chosen are shown in Figure 1. The blended system of 5 M DEEA–2 M MAPA (Figure 2(a)) can form two liquid phases (Figure 2(b)) after being loaded with CO₂, one lean in CO₂ and one rich in CO₂, and can, after absorption, be separated based on differences in density. Nuclear magnetic resonance (NMR) studies have shown that the lower phase, rich in CO₂, has more peaks that belong to the carbamate formed from the MAPA, whereas a peak at 162.6 ppm is assigned to HCO₃[−]/CO₃^{2−}. The peaks in the blue spectrum belong to DEEA in which the carbamate peaks are almost invisible, indicating that this upper phase is lean in CO₂ and rich with DEEA (Figure 2). The ratio of DEEA/MAPA in the lower phase increases with increasing partial pressure, whereas for the upper phase the opposite is true. Only the heavy phase, rich in CO₂ loading, is sent to the stripper.³⁰ The proposed solvent combination, DEEA/MAPA, may lead to lower energy requirements compared to 30 wt.% MEA and the overall efficiency penalty may be significantly lower.

More recently, Xu and his colleagues have utilized a solution of 1,4-Butanediamine (BDA) and DEEA to absorb CO₂. The mixed solution separates into two phases upon CO₂ absorption due to the limited solubility of DEEA and the fast reaction rate of BDA with CO₂, and most of the CO₂ is stored in the lower phase (Figure 3(a) and (b)).³¹ Analysis of the reaction products has shown that the products are mainly carbamates in the upper

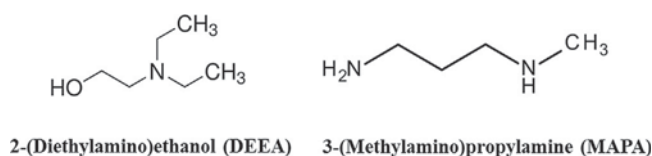
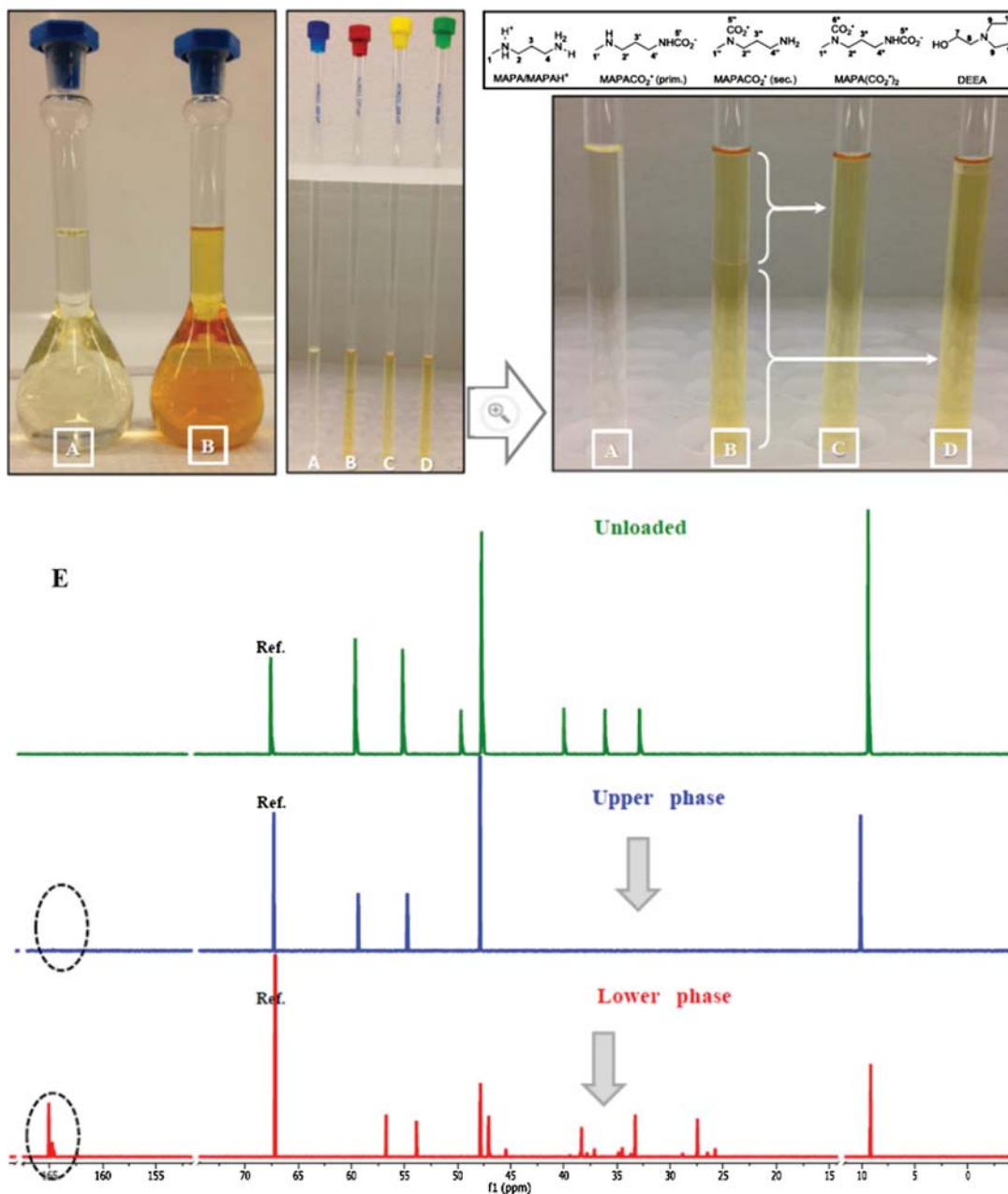


Figure 1
Chemical structures of DEEA and MAPA.

**Figure 2**

NMR tubes of DEEA-MAPA-H₂O systems: (A) unloaded, (B) loaded (2 phases formed), (C) upper phase, and (D) lower phase. (E) ¹³C NMR spectrum of the two-liquid phase system of the DEEA/MAPA system, green (gray in print versions) spectra—unloaded, blue (dark gray in print versions) spectra—upper phase and red (light gray in print versions) spectra—lower phase. The arrows and circles denote the carbamate peaks.¹⁷

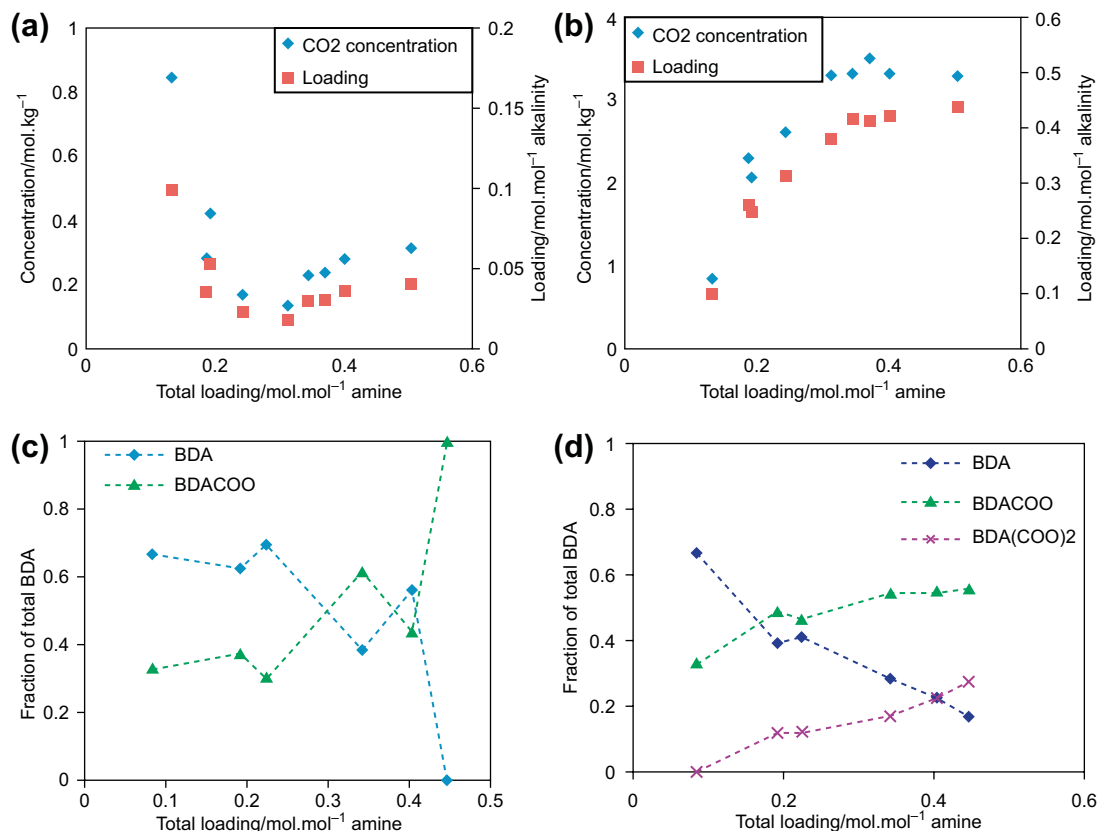


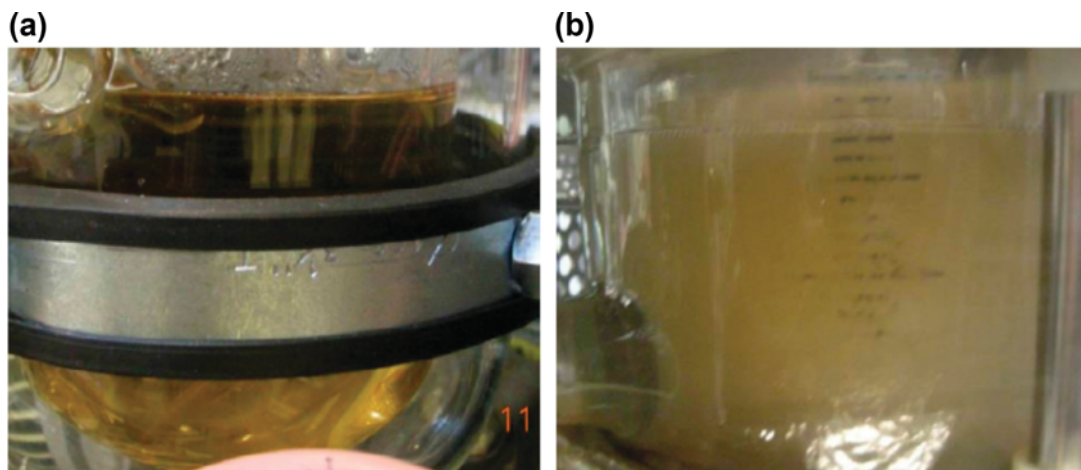
Figure 3

(a–b) The relationship of the CO₂ concentrations with total loading of the 17 samples in the (a) upper and (b) lower phase, respectively. (c–d) Mole fractions of the species in the lower phase in the (c) upper and (d) lower phase, respectively.³¹

phase, whereas the mole fractions of BDA, carbamate, and bicarbamate are 16.8, 55.8, and 27.4%, respectively, in the lower phase; the total loading is 0.446 mol/mol amine (Figure 3(c) and (d)).

4.2 Lipophilic-Amine-Based Thermomorphic Biphasic Solvents

Lipophilic amines, such as the tertiary amine *N,N*-dimethylcyclohexylamine (DMCA) and the secondary amine dipropylamine (DPA), exhibit a thermomorphic phase transition (i.e., thermal-induced miscibility) upon heating, giving rise to autoextractive behavior. Such behavior enhances desorption at temperatures well below the solvent boiling point.³² Such thermomorphic biphasic solvent (TBS) systems have low regeneration temperatures (less than 80 °C) and high cyclic CO₂-loading capacity (e.g., 0.9 mol CO₂/mol absorbent).³³

**Figure 4**

(a) Biphasic solvent in one phase at the bottom of the absorber. (b) Biphasic solvent in two phases in the regenerator.³⁵

The organic phase that is formed acts as an extractive agent, removing the amine from the aqueous phase and driving the reaction toward dissociation of the carbamate and bicarbonate species in the loaded aqueous phase according to Le Chatelier's principle. Compared to MEA, selected lipophilic amines have shown potential advantages in CO₂ loading, solvent regenerability, and chemical stability. The low temperature (~ 80 °C) for desorption also permits the use of waste heat for reducing the operating cost.³⁴ Such biphasic solvent systems have been evaluated in a benchmark unit that comprises an absorber column (2.5 cm in diameter and 145 cm in height) filled with high efficiency and structured packing and a 500 ml stirred tank as a regenerator (Figure 4). Three solvent formulations have been tested at various regeneration temperatures ranging from 50 to 95 °C. A full recovery can be obtained with certain solvent formulations at a regeneration temperature around 90 °C with a total gas flow rate of 300 NI/h (85% N₂ and 15% CO₂). In the subsequent improved process (Figure 5), deep regeneration is enhanced by liquid–liquid phase separation, which permits exploitation of the low-value heat at ~ 90 °C from the other processes, and can cut energy consumption by more than 35% compared to the conventional MEA solvent systems.³⁴

4.3 DMX Solvents

Another CO₂ capture technology has been developed by IFP Energies nouvelles based on liquid–liquid phase separation.²⁰ Several solvents have been studied at IFP Energies nouvelles, such as 1,3-dipropyl-methyl-xanthine (DMX)-1 solvent, which shows a high capacity of CO₂ absorption, good stability toward potential degradation, low corrosion,

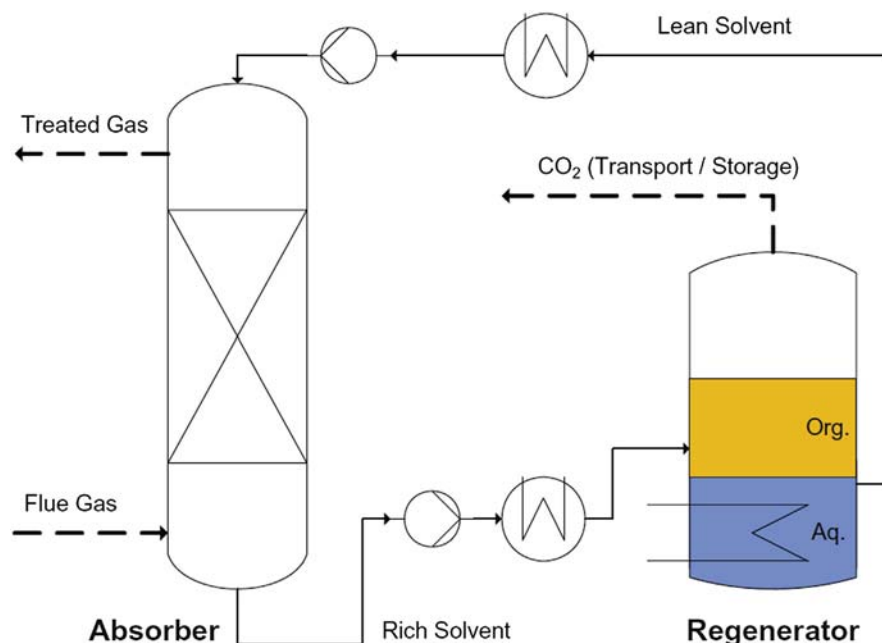
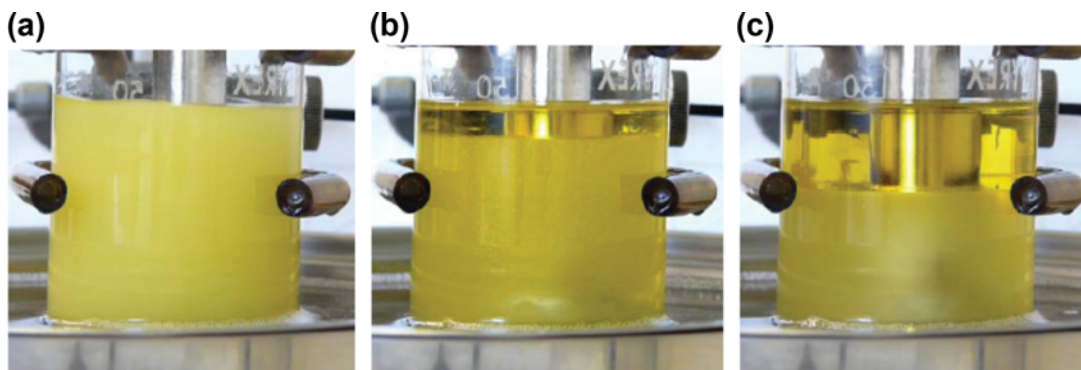


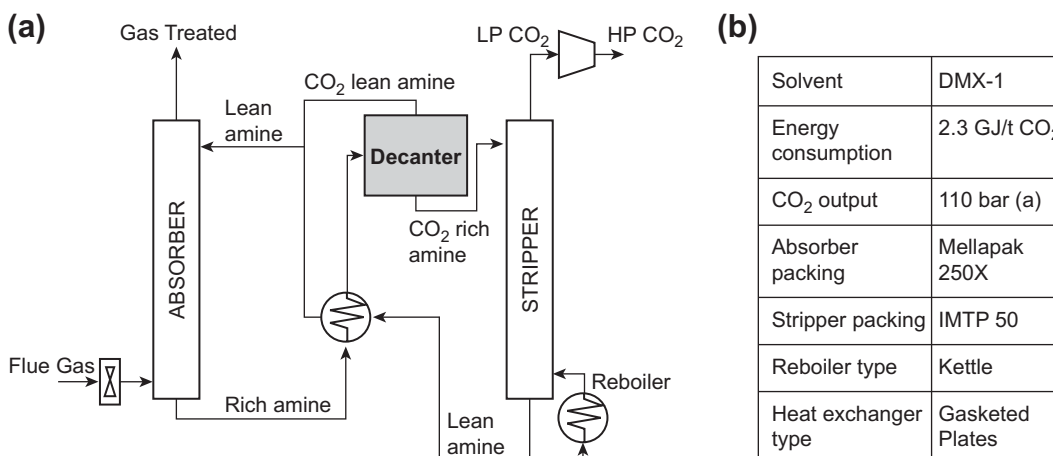
Figure 5

Simplified process flow sheet for the TBS system.³⁴

and fast separation of the two phases. After CO_2 absorption, the DMX-1 solvent is stirred with an Ultra-Turrax homogenizer (2.5 cm diameter for a 6 cm diameter cell) at 11,000 rpm in a stirred cell. Once the Ultra-Turrax is stopped, the liquid/liquid interfaces are formed. Under the operating conditions corresponding to the pictures in Figure 6, the decantation of the different phases can occur in less than 1 min. One can see that the light phase is limpid, whereas the dense phase is opaque. In this process, the dispersion of the heavy phase in the light phase should be avoided because the heavy phase, which contains the most CO_2 , needs to be regenerated. In general, composition of the two liquid phases depends on various parameters like amine concentration in the solvent, CO_2 partial pressure, or temperature. Figure 7(a) shows a possible configuration for the process flow diagram. The DMXTM solvent process differs from the MEA process mainly by having an additional operation unit for decantation. The decanter is preferably positioned after the amine/amine heat exchanger and before the regenerator. This unit operation exploits the liquid/liquid separation property of the solvent with the simultaneous effect of CO_2 charge and heat. Only the dense phase having a high CO_2 concentration is injected in the regenerator, whereas the light phase, without being regenerated, is mixed with the regenerated solvent coming from the stripper and is subsequently reinjected into the absorber.²⁰ Separation of the phases allows reduction in the liquid flow rate in the stripper, and thus reduces the energy requirement for regeneration of the solvent. Process

**Figure 6**

Stirred-cell tests for the DMX-1 solvent: system at (a) $t = 0$ s, (b) $t = 15$ s, and (c) $t = 40$ s.²⁰

**Figure 7**

(a) Simplified process flow diagram of the IFP energies nouvelles DMX™ process and (b) corresponding main process characteristics.²⁰

simulations (Figure 7(b)) show that the DMX™ solvent process can result in a significant reduction in energy consumption compared to 30 wt.% MEA; the energy consumption decreases from 3.7 GJ/ton CO₂ (30 wt.% MEA) to 2.3–2.1 GJ/ton CO₂.²⁰

4.4 Self-Concentrating 3H Amine Absorbents

The 3H Company (3H) has been leading an integrated process team to conduct research using their proprietary self-concentrating amine absorbents for CO₂ capture from coal-fired power plants.³⁶ The technology removes CO₂ from power-plant flue gases using an amine absorbent and a matched nonaqueous solvent that, when reacted with CO₂,

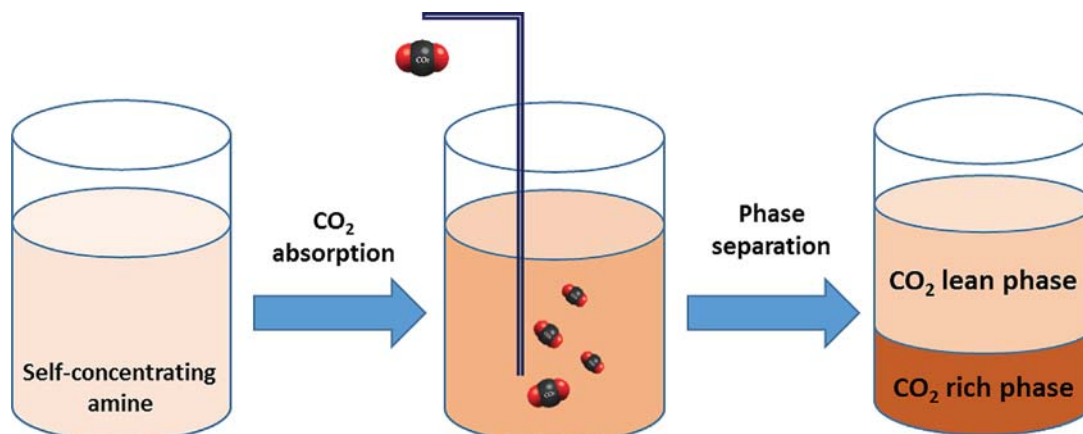


Figure 8

Concept of 3H's self-concentrating amine absorbent process.

rapidly forms two distinct liquid phases: a CO₂-rich phase and a CO₂-lean phase (Figure 8). Only the CO₂-rich phase undergoes regeneration to remove the CO₂ and recycle the solvent. Regeneration of this significantly smaller CO₂-rich phase volume, lower heat capacity, and less heat of vaporization of the nonaqueous solvent, is expected to reduce the energy required for the self-concentrating capture process. The technology may potentially increase the amine CO₂ absorption rate and reduce the energy penalty associated with regeneration compared to conventional MEA-based processes. Additionally, the absorbent is stable in the flue gas environment. Its other attributes include high absorption rate, high CO₂ loading and working capacity, low regeneration temperature and heat requirement, low heat of reaction with CO₂, low corrosion on steel, and low amine loss and degradation. Initial bench-scale work has shown that this process is able to significantly reduce the cost of energy consumption. In addition, the absorbent is able to significantly reduce corrosion of carbon steel, and amine degradation and loss. The technology can also be used in other industries representing large point source of CO₂ release, such as petroleum, chemical, steel, food, and other industries for CO₂ capture or separation.

4.5 Alkanolamine/IL Emulsions

ILs have been proposed as attractive alternatives for CO₂ capture because they have negligible volatility, nonflammability, high thermal stability, and virtually unlimited chemical tunability. However, these properties alone do not appear competitive enough when compared to gas-capture efficiency of aqueous alkanolamine systems. Coupling the advantages of alkanolamines with those of room-temperature ILs (RTILs) might provide a better route for cost-efficient practicable CO₂ capture.³⁷

Hasib-ur-Rahman et al. have evaluated a phase-change solvent by making use of diethanolamine (DEA)/1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide emulsions (Figure 9). This phase-change solvent can capture CO₂ up to the stoichiometric maximum through crystallizing CO₂-captured product (DEA-carbamate) while avoiding equilibrium limitations.¹⁶ Precipitation of carbamate has also been found during the CO₂ absorption process involving ILs like 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]), 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf₂N]), and 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([HMIM][Tf₂N]). The solid phase (precipitates) quickly rises to the surface, which makes it easy to separate (Figure 10(a)–(c)). The hydrophobicity of ILs and the density differences (between solid and liquid phases) are believed responsible for the carbamate crystallization and the rising of carbamate crystals from the liquid. The hydrophobic nature of ILs seems to play a major role in the segregation of solid products from the fluid phase. This is evident from the carbamate orientation in the [HMIM][Tf₂N]-based system; in surfactant (Triton[®] X-100)-stabilized emulsion, the carbamate product remains dispersed in the suspension (Figure 10(d)). CO₂ absorption tests show that gas-loading capacity up to the stoichiometric maximum (0.5 mol of CO₂ per mole of DEA) can be achieved. Thermogravimetric analysis does not show much variation in CO₂ uptake rate among the three emulsion types studied (Figure 10(e)). The crystallization of the carbamate product, the structural unit of which is composed of protonated-DEA cation and DEA-carbamate anion (Figure 10(f)), enables the process to reach completion while avoiding any equilibrium limitations specifically faced in aqueous amine systems. Phase separation of the solvents also provides easy separation,

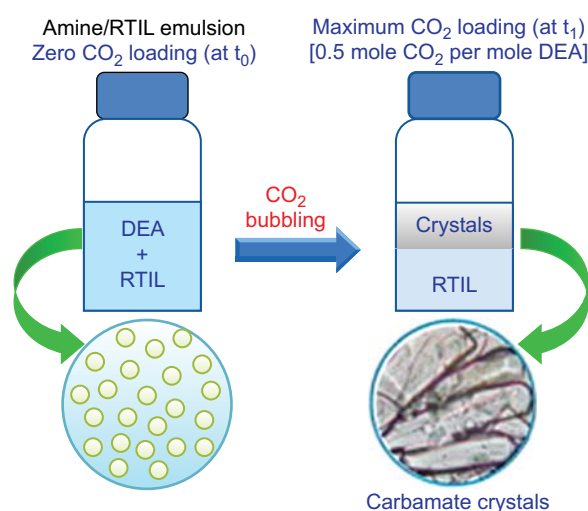
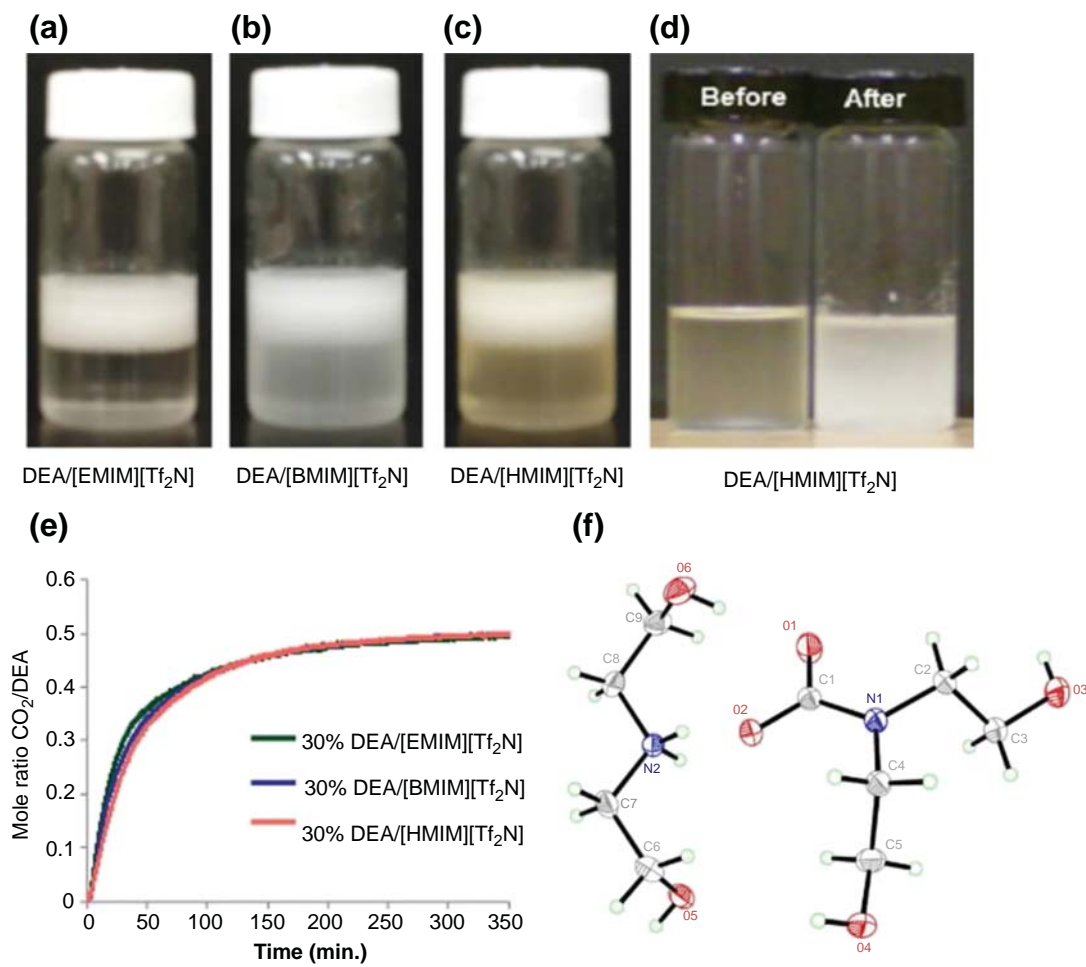


Figure 9

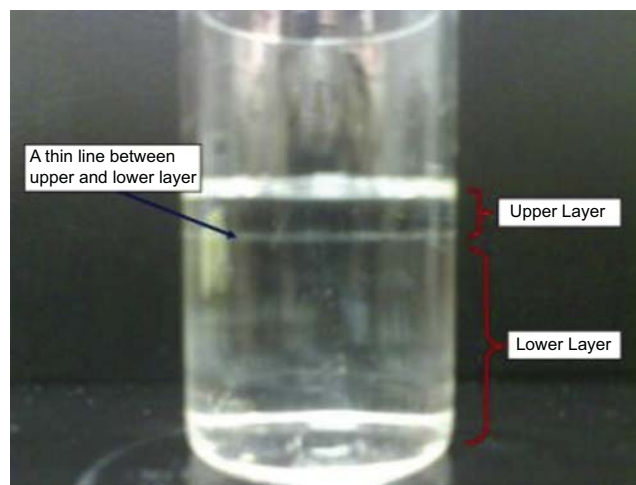
Immiscible alkanolamine/RTIL system for efficient CO₂ capture.¹⁶

**Figure 10**

DEA/RTIL system for CO₂ capture: (a–c) (without surfactant) after CO₂ capture; (d) (with surfactant) before and after CO₂ capture; (e) CO₂ capture capacity profiles of the DEA/RTIL system at atmospheric pressure and 25 °C; (f) basic structural unit in DEA-carbamate (C₉H₂₂N₂O₆) crystal.¹⁶

thereby offering the advantage of regenerating a smaller (solid carbamate) volume with less energy consumption.

In addition, phase separation has been found in aqueous solutions of N-methyldiethanolamine (MDEA) and guanidinium tris(pentafluoroethyl) trifluorophosphate [gua]⁺[FAP][−] IL after the absorption of CO₂ at high pressures. Aziz and his coworkers have observed the formation of double-layer solvents after CO₂ absorption (Figure 11) and shown that amine-IL mixtures could be easily regenerated.³⁸

**Figure 11**

A photo of double-layer CO₂-rich mixtures.³⁸

4.6 Chilled Ammonia

Under dry conditions, ambient temperature, and atmospheric pressure, the reaction of CO₂ and ammonia is exothermic and produces ammonium carbamate. Such a reaction is not suitable for practical CCS applications, because the reaction rate of CO₂ and NH₃ in the gas phase is low, the loss of NH₃ is significant, the CO₂ removal efficiency is low, and the removal of solid ammonium carbamate from the absorbent reactor is difficult.³⁹ However, if the reaction takes place in a liquid phase, it would facilitate the process and make it easy to separate the solids from the solution, thereby allowing an efficient recycling of the unreacted scrubbing solution. Based on this idea, the chilled ammonia process was developed using ammonia to absorb CO₂ at low temperatures (2–10 °C). The low-temperature process has the advantages of decreasing the ammonia slip in the absorber and decreasing the flue-gas volume.⁴⁰ Barzagli and coworkers have observed the precipitation of pheromone in the ethanol-water chilled-ammonia solution after CO₂ absorption.⁴¹ The process has led to the formation of solid mixtures of ammonium bicarbonate and ammonium carbamate, or of ammonium carbamate alone. Selective precipitation of ammonium carbamate can be achieved by reacting gaseous CO₂ and NH₃ in anhydrous ethanol, 1-propanol, and *N,N*-dimethylformamide (DMF) in a flow reactor that operates continuously. The unreacted ammonia solution, once separated by filtration from the solid compounds, can be completely reclaimed into the absorbent reactor. The ammonium carbamate obtained has been used to produce urea at 393–413 K in the presence of Cu(II) and Zn(II) catalysts, and good yields (up to 54% on carbamate basis) have been achieved. The chilled ammonia process has the potential to be applied

to capture CO₂ from flue gases exhausted from coal-fired boilers and natural gas combined-cycle systems, as well as a wide variety of industrial applications.⁴²

4.7 Triethylenetetramine (TETA)/Ethanol Solutions

Zheng et al. have reported that triethylenetetramine (TETA) dissolved in ethanol can produce a solid precipitate after CO₂ absorption (Figure 12(a) and (b)), which can then be easily separated and regenerated.¹⁹ In comparison, a TETA/water solution does not form any precipitates after CO₂ absorption. The TETA/ethanol solution offers several advantages for CO₂ capture in regard to absorption rate, absorption capacity, and absorbent regenerability. Both the rate and capacity of CO₂ absorption with the TETA/ethanol solution are significantly higher than those of a TETA/water solution. This is because ethanol cannot only promote the solubility of CO₂ in the liquid phase but can also facilitate the chemical reaction between TETA and CO₂. This approach is found able to

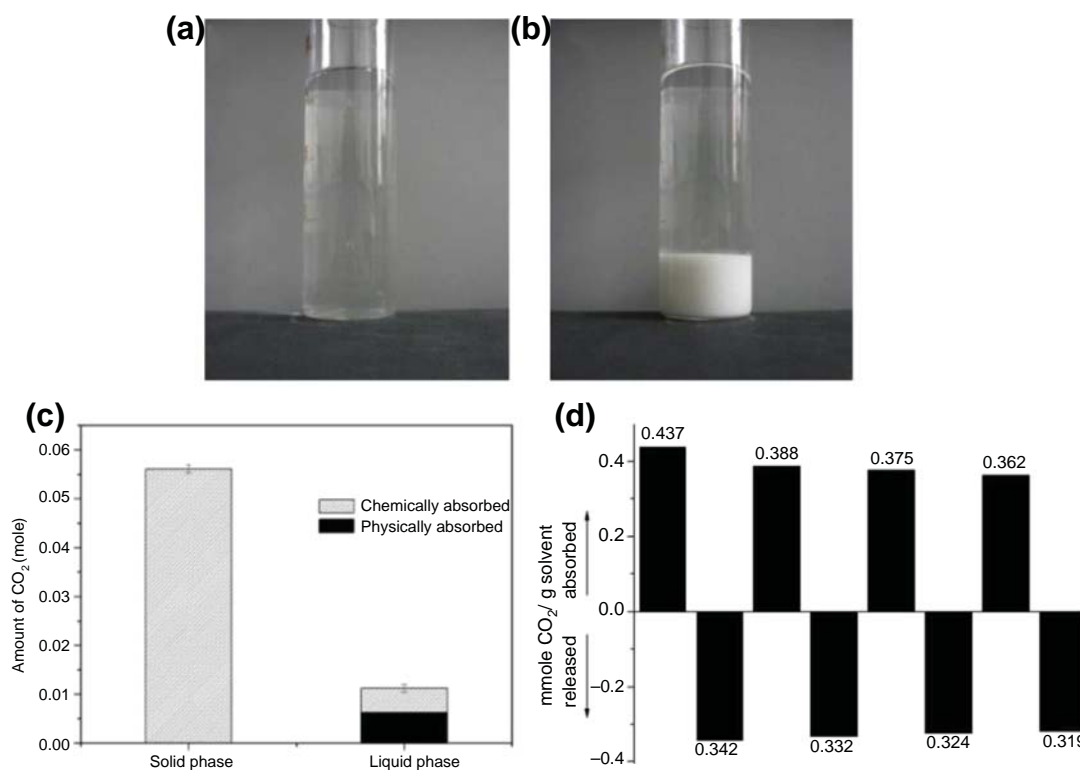


Figure 12

TETA/ethanol solution (a) before CO₂ absorption and (b) after CO₂ absorption. (c) Partition of carbon dioxide in the solid phase and liquid phase. (d) Cycling absorption/regeneration runs of TETA/ethanol solution for CO₂ absorption.¹⁹

capture 81.8% of the absorbed CO₂ in the solid phase as TETA-carbamate (Figure 12(c)). The absorption–desorption tests using a temperature-swing process reveals that the absorption performance of the TETA/ethanol solution is relatively stable (Figure 12(d)). One limitation of using the TETA/ethanol solution for CO₂ removal is that ethanol is a solvent with a high vapor pressure and measures must be taken to mitigate solvent evaporation.

4.8 Phase Change Amino Acid Salt Solvents

Amino-acid salts are of great interest as potential solvents for CO₂ capture because they are considered environmentally friendly. Their prospects are strengthened by the fact that they are naturally present in the environment, and their ionic nature conveniently makes them less volatile.^{43–45} In addition, amino-acid salt solutions have good resistance to an oxygen-rich flue-gas stream. The reactivities of amino-acid salts are similar to those of alkanolamines due to the presence of identical amino functional groups in their molecules. Some amino-acid salts, particularly the potassium salts of glycine, sarcosine, and proline, have faster reaction kinetics with CO₂ than does MEA.^{18,46}

Interestingly, several amino-acid salts can precipitate after absorbing CO₂ to a certain value.⁴⁷ For instance, precipitate formation has been observed during absorption of CO₂ in 2.5 M aqueous potassium salts of N-methylalanine, DL-alanine, and α -aminoisobutyric acid (and its sterically hindered derivatives) at 295 ± 0.5 K.⁴⁸ Different precipitate types may be obtained depending on the amino-acid structure and solubility. Amino acids with a primary amino group, such as taurine, precipitate only the zwitterion species.⁴⁹ Amino acids with a hindered amino group and relatively high zwitterion solubility, such as proline,¹⁰ may precipitate potassium bicarbonate.

Independent of the precipitate type, the formation of a solid reaction product during absorption and its removal from the solution phase by precipitation shifts the reaction equilibrium toward the production of more products (carbamate or bicarbonate). Due to this phase-change phenomenon, the equilibrium CO₂ pressure remains constant while the CO₂-loading of the solvent further increases, so that the driving force for absorption can be maintained at a high level even at high loadings. This significantly improves the absorber performance. This effect has been indicated in Figure 13 (enhanced absorption), in which the possible precipitating species are highlighted. Furthermore, the high loadings lead to reduced energy consumption during regeneration.⁵⁰ In Figure 14, a hypothetical plot is given to depict the difference between a precipitating-based process and a conventional absorption process. This figure shows that for a given partial pressure of CO₂, a process with precipitation has higher loading than a process without precipitation. Therefore, the combined process (simultaneous absorption and precipitating process) leads to additional capacity of the solvent.

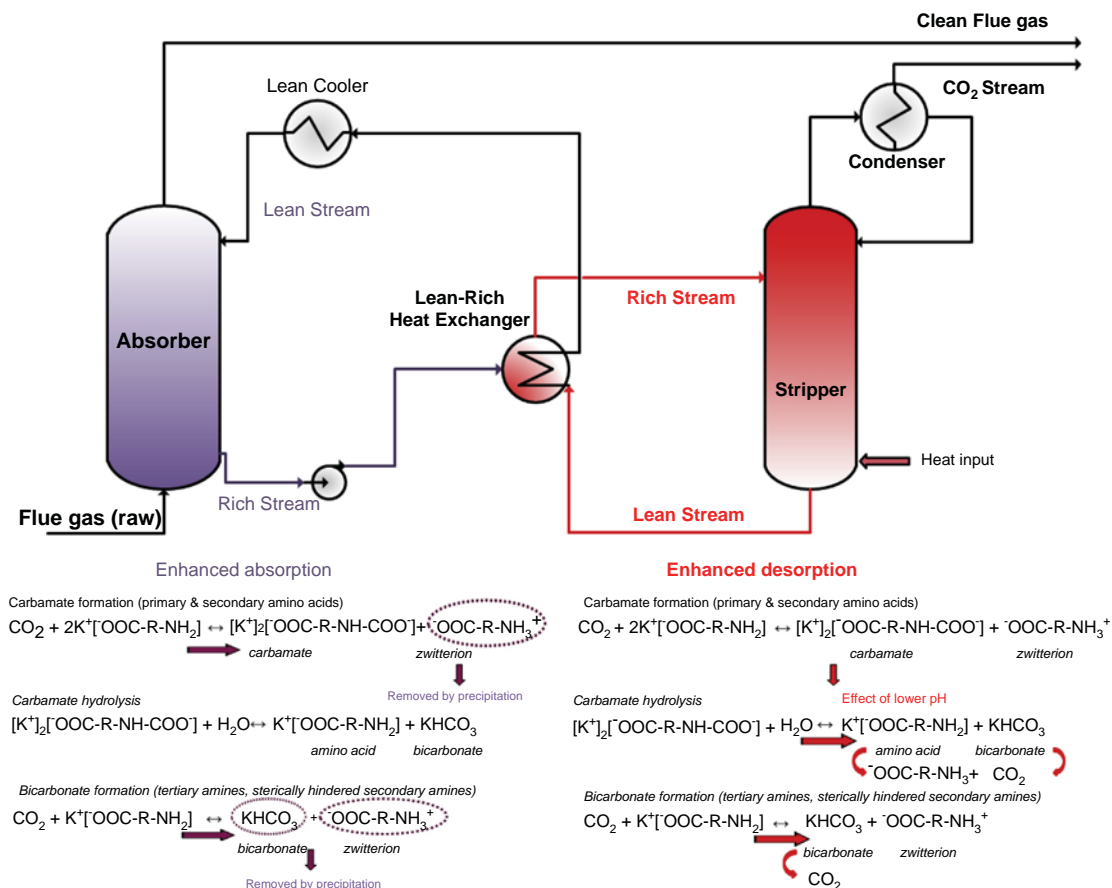


Figure 13

Conventional amine-based process for CO₂ capture in which the reactions specific to amino-acid salts have been added at the bottom of the absorber and the stripper. Besides the heat input necessary to regenerate the solvent, in the case of precipitating amino acids two more effects are possible: Enhanced absorption purple (light gray in print versions) due to the precipitation of reaction products during absorption and enhanced desorption red (gray in print versions) due to a lower pH that results from increasing the amino acid to K⁺ ratio in solution.⁵¹

5. Perspective and Conclusions

Energy- and cost-efficient separation of CO₂ from postcombustion flue gases is a significant technical challenge. Phase-change solvents seem to be a promising new approach by combining the advantages of both solvents and sorbents. One of the biggest challenges related to the applications of phase-change solvents would be the process design, which would need to be able to handle solids/precipitates. Process designs like the ones (i.e., DECAB process, DECAB Plus process) proposed for phase-change amino-acid salt solvents by Fernandez et al. may be adapted for other phase-change systems. As an

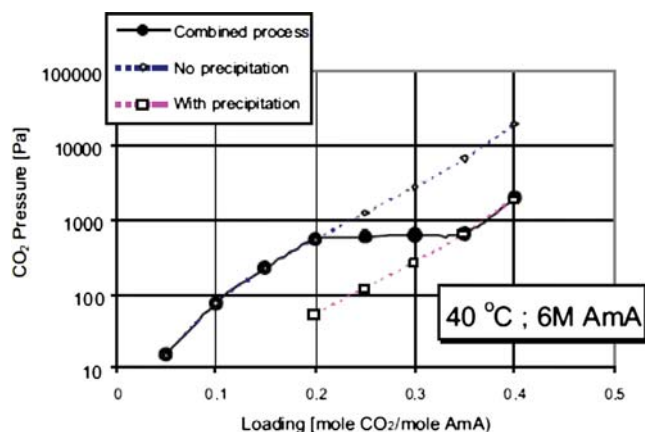


Figure 14

Schematic picture to depict the difference between a precipitating and a nonprecipitating system in terms of CO₂ pressure as a function of loading.⁵²

example, Figure 15 shows the schematic representation of the DECAB process concept for phase-change amino-acid salt solvents.⁵¹ The flue gas (at 40 °C) is contacted with preloaded solvent in a spray tower. The solvent is sprayed as fine droplets with a high surface area for contacting the gas with the solvent. Because of this contact, the CO₂

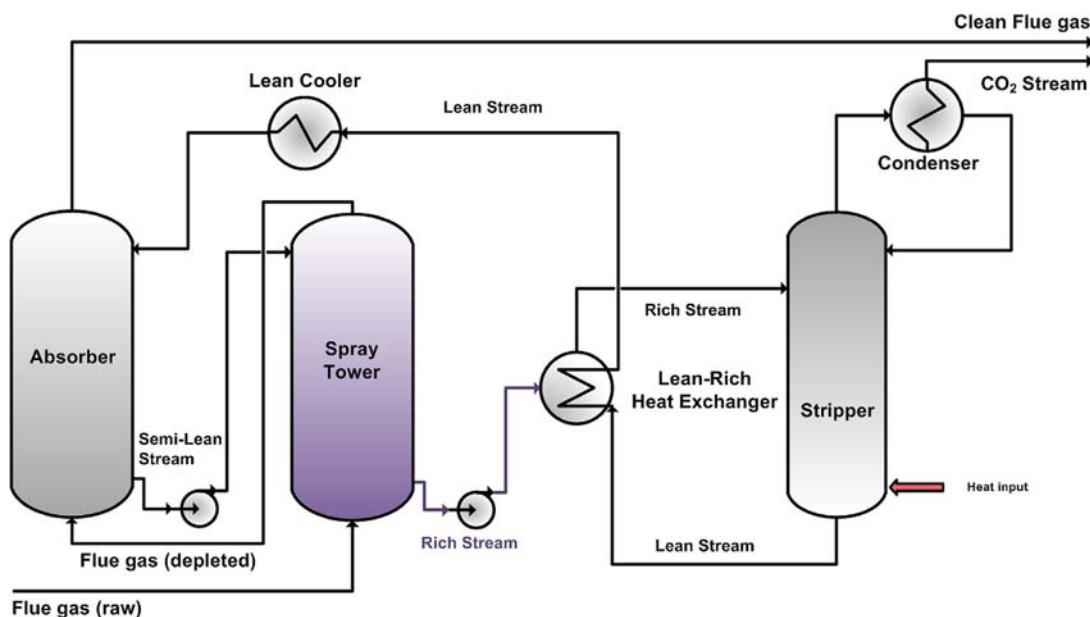


Figure 15

DECAB process concept for CO₂ capture. Enhanced absorption due to the precipitation of reaction products during absorption is highlighted in purple (dark gray in print versions).⁵¹

undergoes a chemical reaction with the solvent that leads to the formation of carbamate and carbonate ions (as shown in Figure 11). Because of this reaction, the pH of the solvent solution decreases and so does the solubility of the amino acid. When the solubility limit is reached, the amino acid precipitates as an amino-acid zwitterion. The resulting solids are collected at the bottom of the tower. The remaining CO₂ in the gas is captured in the absorption column, in which the depleted flue gas is contacted with lean solvent. The absorption column is a conventional packed-absorption column filled with structured packing. There, the CO₂ partial pressure is reduced to the desired value for 90% CO₂ removal. The rich stream containing the solids is further processed in the stripper, via the lean–rich heat exchanger, to release the CO₂. The lean–rich heat exchanger also needs to be of a suitable type to handle solids (e.g., spiral heat exchanger).

In summary, we have reviewed the recent progress in developing phase-change solvents with potential applications for CO₂ removal. Most of these technologies are still at the laboratory research stage, and there remain challenges associated with the scale-up of these technologies to meet the needs of the power generation industry. Future efforts should be focused on developing basic theoretical and mechanistic understandings of phase-change phenomena, to perform pilot plant testing to generate design parameters and process requirements, and to create parallel techno-economic plant design packages for such phase-change solvents.

Acknowledgments

This technical effort was performed in support of the U.S. Department of Energy, National Energy Technology Laboratory's on-going research in carbon management under RES contract DE-FE0004000. Support from WV NASA EPSCoR is also acknowledged. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the funding agencies or their institutions. The authors thank Suzanne Danley for proofreading.

References

1. D'Alessandro DM, Smit B, Long JR. Carbon dioxide capture: prospects for new materials. *Angew Chem Int Ed* 2010;**49**:6058–82.
2. Figueroa JD, Fout T, Plasynski S, McIlvried H, Srivastava RD. Advances in CO₂ capture technology-The U.S. Department of Energy's Carbon Sequestration Program. *Int J Greenhouse Gas Control* 2008;**2**:9–20.
3. Lin L-C, Berger AH, Martin RL, Kim J, Swisher JA, Jariwala K, et al. In silico screening of carbon-capture materials. *Nat Mater* 2012;**11**:633–41.
4. Wang X, Akhmedov NG, Duan Y, Luebke D, Hopkinson D, Li B. Amino acid-functionalized ionic liquid solid sorbents for post-combustion carbon capture. *ACS Appl Mater Interfaces* 2013;**5**:8670–7.
5. Miller MB, Bing W, Luebke DR, Enick RM. Solid CO₂-philes as potential phase-change physical solvents for CO₂. *J Supercrit Fluids* 2012;**61**:212–20.
6. Kim SH, Kim KH, Hong SH. Carbon dioxide capture and use: organic synthesis using carbon dioxide from exhaust gas. *Angew Chem Int Ed* 2014;**53**:771–4.

7. Duan YH, Pfeiffer H, Li BY, Romero-Ibarra IC, Sorescu DC, Luebke DR, et al. CO₂ capture properties of lithium silicates with different ratios of Li₂O/SiO₂: an ab initio thermodynamic and experimental approach. *Phys Chem Chem Phys* 2013;**15**:13538–58.
8. Hedin N, Chen LJ, Laaksonen A. Sorbents for CO₂ capture from flue gas-aspects from materials and theoretical chemistry. *Nanoscale* 2010;**2**:1819–41.
9. Li B, Duan Y, Luebke D, Morreale B. Advances in CO₂ capture technology: A patent review. *Appl Energ* 2013;**102**:1439–47.
10. Majchrowicz ME, Brilman DWF, Groeneveld MJ. Precipitation regime for selected amino acid salts for CO₂ capture from flue gases. *Energy Procedia* 2009;**1**:979–84.
11. Wang X, Akhmedov NG, Duan Y, Luebke D, Li B. Immobilization of amino acid ionic liquids into nanoporous microspheres as robust sorbents for CO₂ capture. *J Mater Chem A* 2013;**1**:2978–82.
12. Jiang B, Kish V, Fauth DJ, Gray ML, Pennline HW, Li B. Performance of amine-multilayered solid sorbents for CO₂ removal: Effect of fabrication variables. *Int J Greenhouse Gas Control* 2011;**5**:1170–5.
13. Li B, Jiang B, Fauth DJ, Gray MML, Pennline HW, Richards GA. Innovative nano-layered solid sorbents for CO₂ capture. *Chem Commun* 2011;**47**:1719–21.
14. Duan YH, Luebke DR, Pennline HW, Li BY, Janik MJ, Halley JW. Ab initio thermodynamic study of the CO₂ capture properties of potassium carbonate sesquihydrate, K₂CO₃ center dot 1.5H₂O. *J Phys Chem C* 2012;**116**:14461–70.
15. Hoshino Y, Imamura K, Yue MC, Inoue G, Miura Y. Reversible absorption of CO₂ triggered by phase transition of amine-containing micro- and nanogel particles. *J Am Chem Soc* 2012;**134**:18177–80.
16. Hasib-ur-Rahman M, Siaj M, Larachi F. CO₂ capture in alkanolamine/room-temperature ionic liquid emulsions: A viable approach with carbamate crystallization and curbed corrosion behavior. *Int J Greenhouse Gas Control* 2012;**6**:246–52.
17. Ciftja AF, Hartono A, Svendsen HF. Experimental study on phase change solvents in CO₂ capture by NMR spectroscopy. *Chem Eng Sci* 2013;**102**:378–86.
18. Ma'mun S, Kim I. Selection and characterization of phase-change solvent for carbon dioxide capture: precipitating system. *Energy Procedia* 2013;**37**:331–9.
19. Zheng S, Tao M, Liu Q, Ning L, He Y, Shi Y. Capturing CO₂ into the precipitate of a phase-changing solvent after absorption. *Environ Sci Technol* 2014;**48**:8905–10.
20. Raynal L, Alix P, Bouillon PA, Gomez A, de Nailly ML, Jacquin M, et al. The DMXTM process : an original solution for lowering the cost of post-combustion carbon capture. *10th international conference on greenhouse gas control technologies* 2011;vol. 4:779–86.
21. Bottoms RR. Separating acid gases. U.S. Patent 1783901; 1930.
22. Bara JE, Camper DE, Gin DL, Noble RD. Room-temperature ionic liquids and composite materials: platform technologies for CO₂ capture. *Accounts Chem Res* 2010;**43**:152–9.
23. MacDowell N, Florin N, Buchard A, Hallett J, Galindo A, Jackson G, et al. An overview of CO₂ capture technologies. *Energy & Environ Sci* 2010;**3**:1645–69.
24. Keith DW, Ha-Duong M, Stolaroff JK. Climate strategy with CO₂ capture from the air. *Clim Change* 2006;**74**:17–45.
25. Brennecke JE, Gurkan BE. Ionic Liquids for CO₂ Capture and Emission Reduction. *J Phys Chem Lett* 2010;**1**:3459–64.
26. Li S, Wang Z, Yu X, Wang J, Wang S. High-performance membranes with multi-permselectivity for CO₂ separation. *Adv Mater* 2012;**24**:3196–200.
27. Perry RJ, Grocela-Rocha TA, O'Brien MJ, Genovese S, Wood BR, Lewis LN, et al. Aminosilicone solvents for CO₂ capture. *ChemSusChem* 2010;**3**:919–30.
28. Bræder P, Svendsen HF. Capacity and Kinetics of Solvents for Post-Combustion CO₂ Capture. *Energy Procedia* 2012;**23**:45–54.
29. Arshad MW, von Solms N, Thomsen K, Svendsen HF. Heat of absorption of CO₂ in aqueous solutions of DEEA, MAPA and their mixture. *Energy Procedia* 2013;**37**:1532–42.

30. Liebenthal U, Pinto DDD, Monteiro JGMS, Svendsen HF, Kather A. Overall Process Analysis and Optimisation for CO₂ Capture from Coal Fired Power Plants based on Phase Change Solvents Forming Two Liquid Phases. *Energy Procedia* 2013;**37**:1844–54.
31. Xu ZC, Wang SJ, Chen CH. CO₂ absorption by biphasic solvents: Mixtures of 1,4-Butanediamine and 2-(Diethylamino)-ethanol. *Int J Greenhouse Gas Control* 2013;**16**:107–15.
32. Zhang JF, Misch R, Tan YD, Agar DW. Novel Thermomorphic Biphasic Amine Solvents for CO₂ Absorption and Low-Temperature Extractive Regeneration. *Chem Eng Technol* 2011;**34**:1481–9.
33. Zhang JF, Nwani O, Tan Y, Agar DW. Carbon dioxide absorption into biphasic amine solvent with solvent loss reduction. *Chem Eng Res Des* 2011;**89**:1190–6.
34. Zhang JF, Qiao Y, Agar DW. Improvement of lipophilic-amine-based thermomorphic biphasic solvent for energy-efficient carbon capture. *6th Trondheim conference on CO₂ capture, transport and storage* 2012;vol. 23:92–101.
35. Zhang J, Agar DW, Zhang X, Geuzebroek F. CO₂ absorption in biphasic solvents with enhanced low temperature solvent regeneration. *Energy Procedia* 2011;**4**:67–74.
36. Hu L. Phase transitional absorption method. US Patent 7,541,011. 2009.
37. Camper D, Bara JE, Gin DL, Noble RD. Room-Temperature Ionic Liquid-Amine Solutions: Tunable Solvents for Efficient and Reversible Capture Of CO₂. *Industrial Eng Chem Res* 2008;**47**:8496–8.
38. Aziz N, Yusoff R, Aroua MK. Absorption of CO₂ in aqueous mixtures of N-methyldiethanolamine and guanidinium tris(pentafluoroethyl)trifluorophosphate ionic liquid at high-pressure. *Fluid Phase Equilib* 2012;**322–323**:120–5.
39. Li XN, Hagaman E, Tsouris C, Lee JW. Removal of carbon dioxide from flue gas by ammonia carbonation in the gas phase. *Energy & Fuels* 2003;**17**:69–74.
40. Darde V, Thomsen K, van Well WJM, Stenby EH. Chilled ammonia process for CO₂ capture. *Int J Greenhouse Gas Control* 2010;**4**:131–6.
41. Barzagli F, Mani F, Peruzzini M. From greenhouse gas to feedstock: formation of ammonium carbamate from CO₂ and NH₃ in organic solvents and its catalytic conversion into urea under mild conditions. *Green Chem* 2011;**13**:1267–74.
42. Mathias PM, Reddy S, O'Connell JP. Quantitative evaluation of the chilled-ammonia process for CO₂ capture using thermodynamic analysis and process simulation. *Int J Greenhouse Gas Control* 2010;**4**:174–9.
43. Knuutila H, Aronu UE, Kvamsdal HM, Chikukwa A. Post combustion CO₂ capture with an amino acid salt. *Energy Procedia* 2011;**4**:1550–7.
44. Liu AH, Ma R, Song C, Yang ZZ, Yu A, Cai Y, et al. Equimolar CO₂ capture by N-substituted amino acid salts and subsequent conversion. *Angew Chem Int Ed* 2012;**51**:11306–10.
45. Portugal AF, Sousa JM, Magalhães FD, Mendes A. Solubility of carbon dioxide in aqueous solutions of amino acid salts. *Chem Eng Sci* 2009;**64**:1993–2002.
46. Jv Holst, Versteeg G, Brilman D, Hogendoorn J. Kinetic study of CO₂ with various amino acid salts in aqueous solution. *Chem Eng Sci* 2009;**64**:59–68.
47. Majchrowicz M, Niederer JPM, Velders AH, Versteeg GF. Precipitation in amino acid salt CO₂ absorption systems. *GHGT-8 NTNU VIDERE. Trondheim (Norway): Springer Berlin/Heidelberg* 2006.
48. Hook RJ. An investigation of some sterically hindered amines as potential carbon dioxide scrubbing compounds. *Industrial Eng Chem Res* 1997;**36**:1779–90.
49. Kumar PS, Hogendoorn JA, Timmer SJ, Feron PHM, Versteeg GF. Equilibrium solubility of CO₂ in aqueous potassium taurate solutions: Part 2. Experimental VLE data and model. *Industrial Eng Chem Res* 2003;**42**:2841–52.
50. Brouwer J, Feron P, Ten Asbroek N. Amino-acid salts for CO₂ capture from flue gases. *Fourth annual conference on carbon capture & sequestration* May 2005.
51. Sanchez-Fernandez E, Mercader FdM, Misiak K, van der Ham L, Linders M, Goetheer E. New Process Concepts for CO₂ Capture based on Precipitating Amino Acids. *Energy Procedia* 2013;**37**:1160–71.
52. Fernandez ES, Goetheer EL. DECAB: Process development of a phase change absorption process. *Energy Procedia* 2011;**4**:868–75.