



Amine-based capture of CO₂ for utilization and storage

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Abstract

Carbon dioxide capture and storage (CCS) technology is an effective CO₂ fixation technology, as documented by the special report produced by Working Group III of the Intergovernmental Panel on Climate Change. Today, this technology has become important due to the threat of global warming and climate change. Furthermore, the development of carbon dioxide capture and utilization (CCU) technology, which reuses the captured CO₂, has been prioritized in recent years to accelerate the deployment of “CCUS.” For both utilization and storage, CO₂ capture is a key process that determines how efficiently decarbonation is able to meet the global target. Regardless of the maturity of various types of CO₂ capture technologies, amines are the most widely used chemical species. This paper contains a brief overview of CCUS followed by a discussion of several aspects of amine-based CO₂ capture technologies.

Global warming

Radiation from the Earth's surface is absorbed by greenhouse gases such as carbon dioxide (CO₂) in the atmosphere. The resulting increase in temperature is equivalent to 30 °C or more globally on average [1, 2]. This means that the Earth's surface temperature would be below 0 °C without greenhouse gases. Global warming is an urgent problem facing our planet due to an increase in greenhouse gases in the atmosphere caused by human activities. The rise in the global average temperature, albeit small compared with the abovementioned natural greenhouse effect, is thought to have serious consequences for various ecosystems [3, 4].

The Swedish physical chemist Svante Arrhenius first proposed that a global temperature rise of several °C could occur due to CO₂ emitted from the use of fossil fuels such as coal and oil [5]. It seems that he slightly overestimated the greenhouse effect of CO₂ while underestimating the increase in human-driven CO₂ emissions. The global warming that we experience today is progressing at a faster rate than Arrhenius' prediction. In 2017, human-induced warming reached approximately 1 °C above pre-industrial levels, increasing at a rate of 0.2 °C per decade [6].

Within the United Nations Framework Convention on Climate Change, the Paris Agreement was adopted in 2015 and entered into force in 2016. Its central aim is to strengthen the global response to the threat of climate change by limiting the increase in the global average temperature to well below 2 °C from pre-industrial levels and pursuing efforts to limit the temperature increase to 1.5 °C [7]. Following the Paris Agreement, the Special Report, Global Warming of 1.5 °C [6], was approved by the Intergovernmental Panel on Climate Change (IPCC) and released in 2018. The report stated that global warming is likely to reach 1.5 °C between 2030 and 2052 if it continues to increase at the current rate.

In 2017, the International Energy Agency (IEA) presented potential energy sector development to 2060, namely, the 2 °C scenario (2DS) and beyond the 2 °C scenario (B2DS). This path of rapid decarbonization is in line with the Paris Agreement [8]. In both 2DS and B2DS, carbon dioxide capture and storage (CCS) and the implementation of renewable energy technologies such as wind, solar, geothermal, and biomass play an indispensable role in achieving these targets.

Carbon dioxide capture, utilization and storage (CCUS)

In recent years, there has been growing interest in carbon dioxide capture and utilization (CCU), a technology for the reuse of captured CO₂ [9–12]. The amount of CO₂

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Table 1 The amount of CO₂ used in 2012

Produced compound	CO ₂ used (Mt/y)
Urea	114
Methanol	8
Formaldehyde	3.5
Dimethyl ether	3
Tert-butyl methyl ether	1.5
Polycarbonates	0.01
Organic carbonates	0.005
Inorganic carbonates	ca. 50

Adopted from ref. [13]

converted into chemicals and other non-chemical applications today is less than 200 Mt/y globally [13]. As shown in Table 1, it has mainly been used for urea production. It should be noted that the current CO₂ demand is significantly less than global energy-related CO₂ emissions (>30 Gt/y) [8]. Hepburn et al. [14] analyzed CO₂ utilization trends and estimated that the utilization potentials of chemicals, fuels, and concrete building materials in 2050 are 300–600 Mt/y, 1000–4200 Mt/y, and 100–1400 Mt/y, respectively.

To limit the amount of CO₂ in the atmosphere in the 1970s, Italian physicist Cesare Marchetti proposed a CO₂ management system in which CO₂ is collected at proper fuel transformation points and transferred into the deep seas [15]. He also proposed that disposal could be performed in the form of permanent underground storage by using exhausted gas fields, oil fields, or similar cavities. Then, the IPCC Working Group III, which is responsible for mitigating climate change, published a special report on CCS in 2005 [16, 17]. CCS is the process of CO₂ separation from industrial and energy-related sources, transportation to a storage location, and long-term isolation from the atmosphere. CCS is widely recognized as an effective CO₂ fixation technology and has grown in importance ever since [18–24].

The special report on CCS has two major chapters on CO₂ storage, namely, underground geological storage and ocean storage. In the former chapter, the global geological storage capacity in oil/gas fields and deep saline formations were estimated to be 675–900 Gt and 10³–10⁴ Gt, respectively [16], indicating that CCS can play a significant role in reducing greenhouse gas emissions. The largest change since then is that ocean storage of CO₂ is no longer considered a viable option [25].

CO₂ capture in large-scale CCS facilities

Among large-scale CCS facilities in the world with a capacity of at least 400,000 t/y, nineteen of them were operating in 2019 [26]. In Table 2, information on the CCS

projects based on the Global CCS Institute (GCCSI) database [27] and additional surveys [28–36] is listed.

The majority of the nineteen CCS facilities capture CO₂ for natural gas processing. The Sleipner CO₂ injection was the world's first industrial offshore CCS project [32, 36]. Natural gas produced in the Sleipner Vest field contains ca. 9% CO₂ and must be reduced to less than 2.5% for the gas to meet specifications prior to being sold. The CO₂ captured with amine scrubbing using aqueous N-methyldiethanolamine (MDEA) solutions containing ca. 2% methane (CH₄) has been injected into a saline aquifer at a rate of approximately 1 Mt/y since 1996. Notably, considering the high global warming potential of CH₄ [37], its effect would be non-negligible if the byproduct of the CO₂ removal process was released into the atmosphere.

In addition to natural gas processing, large-scale CCS facilities are currently in operation for chemical, hydrogen (H₂) and steel production as well as power generation. CO₂ capture from fossil fuel power plants has some technical hurdles based on the characteristics of exhaust gas: relatively low CO₂ partial pressure, the presence of significant amounts of oxygen (O₂), and impurities such as sulfur oxides (SO_x) and nitrogen oxides (NO_x) [38–40]. Unit 3 at the Boundary Dam power station in Saskatchewan is the world's first commercial-scale CCS process on a coal-fired power plant [32, 35]. The retrofit with a capture capacity of approximately 1 Mt-CO₂/y is based on regenerable amine technology by Shell Cansolv. It was designed to allow the installation of CCS equipment that would convert Unit 3 into a reliable long-term producer of clean base-load electricity. Simultaneously, the captured CO₂ is used for enhanced oil recovery (EOR) [41, 42] in the province. The Petra Nova project [32, 35] is the world's largest post-combustion CO₂ capture system with a capture capacity of 1.4 Mt-CO₂/y. It has been in operation since 2017 and uses a proprietary amine solvent, KS-1, which was developed by the Kansai Electric Power Co. and Mitsubishi Heavy Industries, Ltd [43]. The captured CO₂ is transported via a pipeline to an oil field for EOR.

In the IPCC special report on CCS [16], CO₂ capture technologies were categorized into three separation methods: separation with sorbents/solvents, separation with membranes, and separation by cryogenic distillation. Among these methods, cryogenic distillation seems to be unsuitable for large-scale CCS. This is because distillation is an energy intensive process with the power requirement estimated to be 600–660 kWh/t-CO₂ due to the extremely low temperature and high pressure of the process [44]. As shown in Table 2, large-scale CCS facilities that are currently in operation mostly adopt the separation with solvents method, i.e., the absorption method.

Solvents for CO₂ capture can be physical solvents such as methanol that absorb CO₂ based on Henry's law or

Table 2 Large-scale CCS facilities in operation

Name	Country	Start	Industry	Capture	
Boundary Dam	Canada	2014	Power	Cansolv	Amine solvents for low pressure CO ₂
Petra Nova	USA	2017	Power	KS-1	
CNPC Jilin	China	2018	NG	MEA	
Sleipner	Norway	1996	NG	MDEA	
Snøhvit	Norway	2008	NG	PZ/MDEA	
Uthmaniyah	Saudi Arabia	2015	NG	Amine	Amine solvents for high pressure CO ₂
Quest	Canada	2015	Hydrogen	PZ/MDEA	
Abu Dhabi	UAE	2016	Iron, Steel	MDEA	
Gorgon	Australia	2019	NG	PZ/MDEA	
Terrell	USA	1972	NG	C ₄ H ₆ O ₃	
Shute Creek	USA	1986	NG	Selexol	Physical solvents for high pressure CO ₂
Great Plains	USA	2000	NG	Rectisol	
Century	USA	2010	Synfuels	Selexol	
Lost Cabin	USA	2013	NG	Selexol	
Coffeyville	USA	2013	Fertilizer	Selexol	
Enid Fertilizer	USA	1982	Fertilizer	K ₂ CO ₃	Others
Air Products	USA	2013	Hydrogen	Adsorbent	
Petrobras	Brazil	2013	NG	Membrane	
Illinois	USA	2017	Ethanol	Capture less	

Based on the GCCSI database [26, 27] and additional surveys [28–36]. NG natural gas processing, C₄H₆O₃ propylene carbonate

chemical solvents that absorb CO₂ through chemical reactions [45]. Physical solvents are suitable for the separation of CO₂ with high pressure. Chemical solvents with relatively low reactivity towards CO₂ are used for gas with high-pressure CO₂, such as syngas, while those with high reactivity can be used for gas with low-pressure CO₂, such as coal-fired flue gas.

Among the large-scale facilities shown in Table 2, nine CCS projects use amine-based chemical solvents such as monoethanolamine (MEA) [46] and MDEA, while six projects use physical solvents [47]. As for the sorbent-based and membrane separation methods, both have been used in one CCS project each since 2013. A sorbent-based vacuum swing adsorption process was retrofitted in steam methane reformers to separate CO₂ from the gas stream with a capacity of approximately 1 Mt-CO₂/y for EOR in Texas [27, 32]. The CO₂-EOR project at offshore oil and gas fields in Brazil has installed UOP Separex membrane systems, which comprise polymeric membrane materials for solution diffusion-based gas permeation. This is carried out to remove CO₂ and water for natural gas processing at approximately 7 Mm³/d [27, 30, 32].

Figure 1 shows the breakdown of the CO₂ captured in the nineteen large-scale CCS facilities. The breakdown was calculated by summing the medians from the GCCSI database [27]. The total CO₂ capacity of all nineteen large-scale facilities reached 35 Mt/y, far less than the amount of reduction required to mitigate global warming [8].

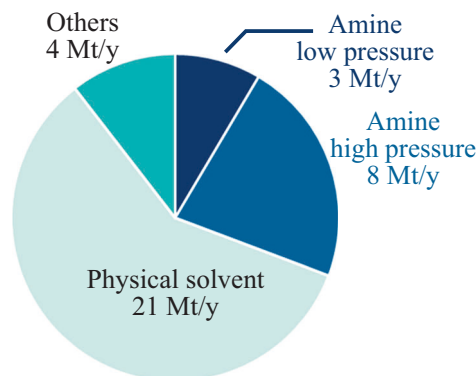


Fig. 1 Breakdown of CO₂ capture amounts in the nineteen large-scale CCS facilities in operation

To accelerate the deployment of CCUS over the next decade, CO₂ capture using amine-based solvents, which is the most effective and mature technology, is of paramount importance. In addition, further process optimization, scaling, and deployments for next-generation CO₂ capture technologies, including sorbent-based and membrane separation technologies [48], are expected in the coming years.

Amine-CO₂ reactions

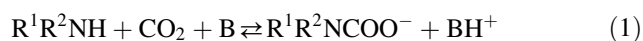
Generally, a CO₂ capture process consists of two steps: (i) separation of CO₂ from a gas mixture through a selective

reaction and (ii) regeneration of the material used for CO₂ separation by a reverse reaction. The material can be reused for CO₂ capture by sequentially repeating steps (i) and (ii). To capture CO₂ efficiently, one practical requirement is “reversibility.” For example, aqueous sodium hydroxide solutions are not suitable for CO₂ capture, as the strong reaction can be regarded as irreversible under normal conditions. Needless to say, materials that interact weakly with CO₂ are also not suitable for the capture process, as the low selectivity and capacity lead to poor CO₂ capture performance. In this respect, another important requirement for a reaction to capture CO₂ is “moderation [48].”

Amines are the most widely utilized chemicals in a variety of CO₂ capture materials, including chemical solvents [49], porous sorbents [50], gels [51], and membranes [52]. The main reason for this is that the moderate interaction allows for an effective separation of amine and CO₂ via a reversible reaction. It should be noted that the optimal reactivity depends on the surrounding molecular environment, operating temperature, pressure, gas composition, required capture performance, and other factors. Due to large variations in amine molecular structure, the CO₂ capture material within the range of moderate reactivity can be further adjusted based on the amine structure and/or blending amines. Such adjusting has been one of the central themes in the development of CO₂ capture technologies [22, 39, 48].

Amines can be classified into three types based on the number of hydrogen atoms attached to the nitrogen atom. Primary, secondary, and tertiary amines contain nitrogen atoms that are covalently attached to two hydrogen atoms, one hydrogen atom, and only non-hydrogen atoms, respectively. Chemical reactivity is often noted as decreasing in the following order: primary (−NH₂) > secondary (>NH) > tertiary (>N−). However, this order varies depending on the electronic and steric effects of all substituents attached to the nitrogen atoms [48]. Chemical reactivity is also governed by the reaction type and reaction field [53]. For instance, the pK_a values representing Brønsted basicity in aqueous solutions for ethylamine, diethylamine, and triethylamine are 10.63, 10.98, and 10.65, respectively [54].

Primary and secondary amines react with CO₂ to form the carbamate anion and protonated amine as follows [55, 56]:



where Rⁿ represents the substituent, such as an alkyl group, and B is the Brønsted base, such as another amine in the system. Carbamic acid may be produced as an intermediate

or byproduct of the amine-CO₂ reaction depending on the substituents and reaction field [57].



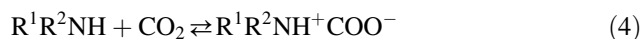
Some amines with hydrophobic phenyl groups absorb CO₂ in the form of carbamic acid rather than carbamate anions [58]. In the presence of water, another major reaction product is the bicarbonate anion [55, 56].



Similarly, the alkyl carbonate anion may form in the presence of alkanols [59].

As substituents drastically affect amine properties, substituent effects have been studied extensively for the development of efficient amine-based materials for CO₂ capture [56, 60–64]. Steric hindrance and hydroxy substituent groups often significantly affect the performance of CO₂ capture [65]. For example, there are reports that the use of isopropyl groups improves amine-based CO₂ capture efficiency for methods with solvents [66, 67], sorbents [68], and membranes [69].

The most well-known intermediate in the amine-CO₂ reaction is zwitterion [70, 71].



In aqueous solutions of alkanolamines such as MEA, carbamate formation (1) occurs via a two-step mechanism, where the zwitterion first forms followed by its deprotonation [72, 73]. Generally, in comparison to other reactions (2) and (3), zwitterion formation (4) exhibits faster reaction kinetics. Therefore, reaction (4) is significant for the mass transfer of CO₂. On the other hand, a bicarbonate anion has the advantage of high diffusivity because of its small size as well as its low energy requirements during the regeneration process [48].

Factors affecting the reactions

There are a wide range of factors that affect amine-CO₂ reactions in CO₂ capture processes. In this section, we focus on CO₂ partial pressure and the reaction field.

The formations of carbamate anion (1) and bicarbonate anion (3) are sometimes compared in terms of stoichiometry. In aqueous amine solutions, the former consumes 2 mols of amine to 1 mol of CO₂, while the latter requires 1 mol of amine to 1 mol of CO₂. However, stoichiometry is only one of the factors that affects the absorption capacity of CO₂. The basic strength, molecular weight, and surrounding environment of amines have a larger influence on the

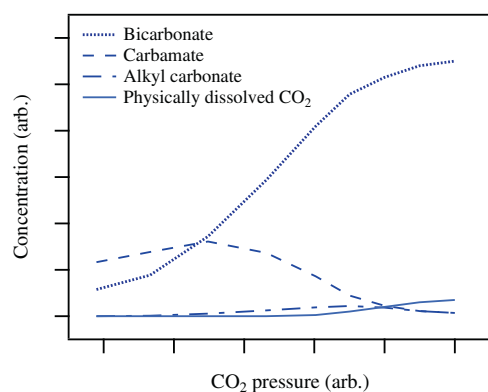
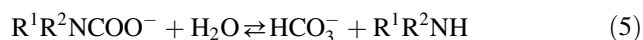


Fig. 2 Schematic distribution of the forms of CO₂ absorbed in an alkanolamine–CO₂–water system

absorption capacity [53, 56]. For instance, the traditional 30 wt% MEA aqueous solution [46], which predominantly forms the carbamate anion for CO₂ absorption, exhibits relatively high CO₂ capacity under post-combustion capture conditions due to the strong basicity and low molecular weight of MEA.

Furthermore, the branching ratio of the carbamate anion, bicarbonate anion, and other chemical forms changes based on CO₂ partial pressure for any primary and secondary amines. Figure 2 is a schematic of the distribution of carbamate, bicarbonate, alkyl carbonate, and physically absorbed CO₂ as a function of the CO₂ partial pressure in an alkanolamine–CO₂–water system. The schematic was based on quantitative measurements at equilibrium [59, 67, 74]. Under lower CO₂ partial pressures, the strongest reaction was predominantly carbamate formation. As the CO₂ partial pressure increases, the concentration of carbamate anion increases up to the point where it starts to saturate. Subsequently, it starts to drop, while the concentration of bicarbonate anion increases steadily. At the molecular level, increasing the proton concentration in the solution facilitates the conversion of carbamate to bicarbonate [75].



The general trend shown in Fig. 2 can be explained by Le Chatelier's principle [76].

The effect of the surrounding environments, i.e., reaction fields, is also an important factor that governs amine–CO₂ reactions, as was previously studied by the author using quantum chemistry [53]. In reactions (1) and (3), the products are charged species, i.e., carbamate, bicarbonate, and aminium ions. The solvation energy of such charged species depends on the polarity of the surrounding media. Thus, water, a solvent with high polarity, can significantly stabilize these charged species. Notably, water molecules are also able to stabilize the charged species due to the hydrogen-bond effect. Recently, a computational study

revealed that solvents with higher hydrogen bond capacity facilitate zwitterion formation [77].

Amine-containing polymeric membranes

To develop next-generation CO₂ capture technology, membrane separation is a promising strategy with numerous advantages: low capital investment, small footprint, ease of scaling up, low energy requirement, simple operation, and low environmental impact [78–81]. As mentioned previously, a polymeric membrane system was installed in a large-scale CCS facility in 2013 [27, 30, 32]. In addition, several projects using amine-based polymeric membrane systems for CO₂ separation are in the pilot phase [82–84].

In addition to CCS, polymeric membrane systems have been commercialized for natural gas sweetening, although they only occupy 5% of the market today [83]. Membranes for natural gas sweetening are usually made from cellulose acetate and polyimide, which typically show a CO₂/CH₄ selectivity of 15–30. Such polymeric membranes separate gases according to the solution-diffusion mechanism, where gas molecules first dissolve in a polymer at the interface and then diffuse across the membrane. One of the challenges of gas separation using polymers is defined by the “Robeson's upper bound [85, 86]” relationship. Generally, the solution-diffusion mechanism affects the trade-off between permeability and selectivity and is governed by the upper bound [87].

An amine in a polymer membrane can be a CO₂ transport “carrier” through the chemical reaction [88]. In particular, CO₂ will first react with the amine carrier at the interface, and then, the reacted CO₂, e.g., HCO₃[−] will diffuse across the membrane, where regeneration occurs due to low CO₂ partial pressure. As such, a membrane, namely, a “facilitated transport membrane” chemically selects and transports CO₂ in addition to the contribution of physical polymer solution diffusion, and it can achieve both high permeability and selectivity beyond Robeson's upper bound [52, 89].

The CO₂ separation mechanism facilitated by the transport polymeric membrane is illustrated in Fig. 3. For this type of membrane, H₂O is necessary for high CO₂ capture performance. It can be sourced from flue gas in the case of post-combustion CO₂ capture. Moreover, the water absorbency of the polymer also governs the capture performance. As shown in Fig. 3, CO₂ will pass through the polymer layer based on both solution diffusion and carrier-mediated diffusion, while other gases, such as nitrogen (N₂), O₂, CH₄, and H₂, can only pass through via a solution-diffusion mechanism. A thin selective polymer layer, high diffusion coefficient, and steep gradient of carrier concentrations across the polymer will positively affect the CO₂ permeate flux, while low solubilities and diffusion coefficients for other gases in the polymer will lead to high selectivity for

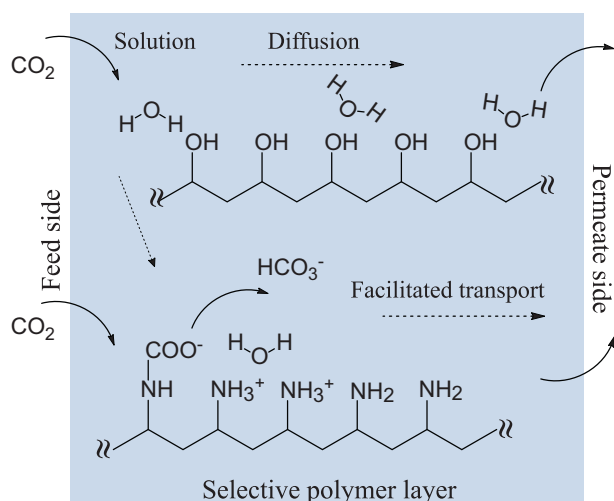


Fig. 3 Mechanism of CO₂ separation by a facilitated transport polymeric membrane

CO₂. For such facilitated transport membranes, poly(amidoamine), poly(vinyl alcohol) (PVA), polyallylamine (PAA), and polyvinyl amine (PVAm) are often applied as selective layers with/without amine additives [48, 83].

Hägg et al. [90, 91] successfully developed facilitated transport membranes using PVAm as a fixed-site carrier (FSC). They evaluated the suitability of FSC for CO₂ transport by examining the effects of feed pressure, relative humidity, acidity of polymer solution (pH), and other factors. They found that the formation of bicarbonate, i.e., reaction (3) or (5), followed by diffusion is crucial for optimal FSC membrane performance [89–94]. Apart from their studies, facilitated transport membranes are usually used under humidified conditions. As described earlier, both carbamate and bicarbonate anions are stabilized by the water solvents. Furthermore, membranes prepared using the acidic polymer solution consisting of PVAm hydrochloride also exhibit moderate selectivity and permeability for CO₂ [92]. Therefore, improved transport of CO₂ through humidification is not solely due to the formation of bicarbonate. Carbamate formation, CO₂ partial pressure and physical solution should also be considered.

As an alternative to FSCs, mobile carriers such as MEA and MDEA have been proposed to improve carrier mobility by incorporating them into a suitable polymer matrix such as PVA [95, 96]. Taniguchi et al. [97] found that the hydroxy group of incorporated alkanolamines could significantly facilitate the transport of CO₂ due to the intramolecular hydrogen bonding effect. In addition to conventional alkanolamines, diamines are also a good alternative for the transport of CO₂ [98, 99]. Wang et al. [99] reported that by incorporating piperazine (PZ) into PVAm, the membrane exhibited a significantly higher CO₂ separation performance than that without PZ.

The effect of diamines is often characterized solely based on the number of amino groups. However, the diamine reaction is more complex than the monoamine reaction. Owing to the significant difference between the pK_{a1} and pK_{a2} values in diamines [100], the respective roles must be assigned to two amino groups to better understand the CO₂ capture mechanism. Previously, Bishnoi and Rochelle [101] confirmed the presence of significant amounts of PZ zwitterions in the PZ–CO₂–water system. With spectroscopic speciation, however, it was difficult to clearly distinguish the two isomers for PZ zwitterion. The author of this review revealed the possible reactions in forming N,N' zwitterions of PZ, as shown in Fig. 4, by performing density functional theory calculations. The results from Gibbs free energy calculations with the SMD/B3PW91/6–311++G(d,p) theory confirmed that the N,N'-zwitterion of PZ is more stable than its two isomers, N,N-zwitterion and carbamic acid of PZ, by 63 kJ/mol and 33 kJ/mol, respectively. This analysis predicts that it will accumulate in the system by CO₂ absorption. More importantly, a stable zwitterion is able to behave both as a Brønsted acid and base. As mentioned previously, a Brønsted acid/base is essential for CO₂ capture. Moreover, the transfer of proton/hydroxide ions is critical for the capture of CO₂. Therefore, these findings for the PZ–CO₂ system indicate that the N,N' zwitterion of PZ is a key component that promotes CO₂ solution-transport-dissolution, enhancing CO₂ capture performance.

Amine-containing polymeric membrane technology for CCUS is now in a pilot testing phase [84]. He et al. [82] developed a pilot installation using PVAm-based FSC hollow fiber membranes at the Tiller plant in Norway. The test results from the feed CO₂ concentration ranging from 9.5% to 12.4% of one stage were obtained as the basis for an optimized two-stage process for actual CO₂ capture. A membrane pilot at the Norcem Cement factory in Norway was also developed for CO₂ capture from flue gas with a high CO₂ content of approximately 17% [102]. In this test, commercial modules from Air Products were utilized. This enabled good stability without significant performance change when exposed to SO₂ and NO_x. Recently, Salim et al. [103] developed pilot-scale spiral-wound modules of PAA-based facilitated transport membranes and tested them at the National Carbon Capture Center in the United States. The field test results for the modules showed good potential for post-combustion CO₂ capture from coal-fired power plants.

Summary and perspective

This study focused on CO₂ capture technologies that have already been used at large-scale CCS facilities, amine-CO₂ chemical reactions for CO₂ capture, and the key mechanisms affecting CO₂ separation performance. Amine-based

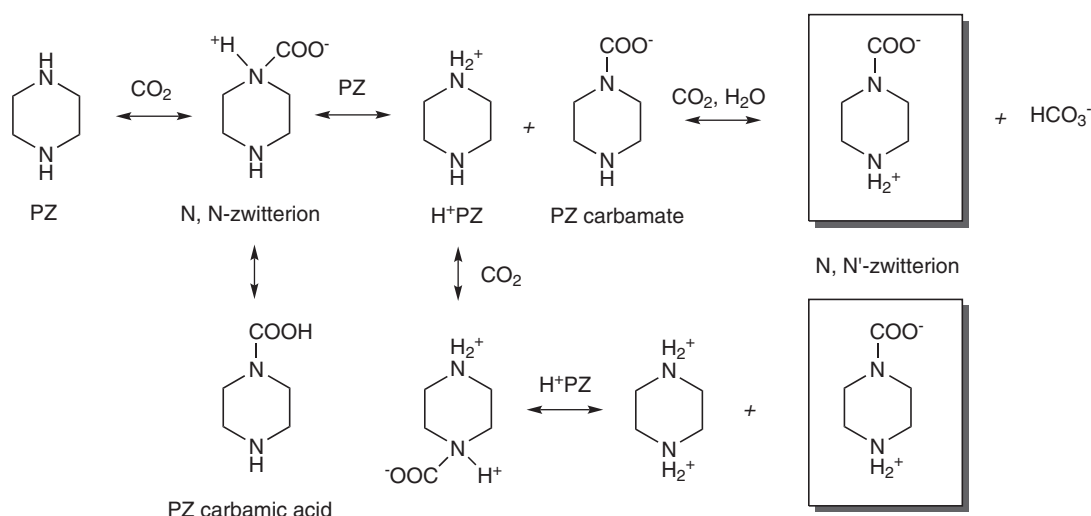


Fig. 4 Reaction pathways to form the N,N'-zwitterion in the PZ–CO₂–water system

CO₂ capture technologies can play a central role in accelerating the deployment of CCUS due to their inherent efficiency, improved performance, and established reliability.

Common problems such as amine degradation, emissions, and environmental impacts [104] have been addressed extensively. Toluene to other gas components, such as SO_x and NO_x, has also been studied. These issues are relevant to not only amines but also matrices such as polymers. To investigate these aspects in detail, long-term field tests using real gas with advanced material analysis technologies will play an important role.

Water management is a relatively new topic in this area. A recent study has shown that water use is an important consideration in the implementation of CCS [105]. Lifecycle assessments of CCUS are also an urgent issue that should be studied further [106]. Materials science will play a crucial role in overcoming the current and emerging challenges.

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Compliance with ethical standards

Conflict of interest The author declares no conflict of interest.

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