Cooperative integration of SCR and CESAR-1, focused on mechanism and performance

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Abstract

Limiting carbon dioxide (CO_2) emissions from large point sources such as thermoelectric plants is a central challenge for mitigating global warming. Among post-combustion capture methods, amine-based absorption using CESAR-1, a blended (AMP) / (PZ) solvent, has been widely used due to its higher CO_2 loading capacity and lower regeneration energy. However, the presence of nitrogen oxides (NO, NO_2) in flue gas imposes a critical limitation: during solvent regeneration, nitrogen oxides promote degradation of CESAR-1, leading to the formation of carcinogenic nitrosamines and nitramines, which are known to be toxic. This paper reviews the distinct characteristics of AMP and PZ, the two components of CESAR-1, as well as the reaction mechanism underlying CO_2 capture in CESAR-1 system. Also, it focuses on the solvent degradation pathway that occurs in the presence of nitrogen oxides, and the mechanism of selective catalytic reduction (SCR). Building on these concepts, we propose an integrated SCR-CESAR-1 system that combines SCR with CESAR-1, an amine-based solvent, to reduce CO_2 emissions while minimizing the risk of undesired byproduct formation. Furthermore, by optimizing the catalyst used in the SCR system, the suggested system aimed to minimize energy consumption across the system.

Keywords

Global warming; Carbon capture; Post-combustion carbon capture; Selective catalytic reduction; CESAR-1

Introduction

Due to rapid industrialization and rising global energy consumption, carbon dioxide (CO_2) levels in Earth's atmosphere have been increasing rapidly. CO_2 accounts for the largest share of human-generated greenhouse gases, and its concentration has continued to increase due to human activities [1], [2]. Not only had its share of greenhouse gas emissions increase over the past 250 years, but the absolute amount of CO_2 has increased as well. This increased CO_2 acts as a significant greenhouse gas, trapping the heat radiated from the Earth [3], [4]. Figure 1 illustrates the historical increase in CO_2 emissions and atmospheric concentrations, particularly since the Industrial Revolution.

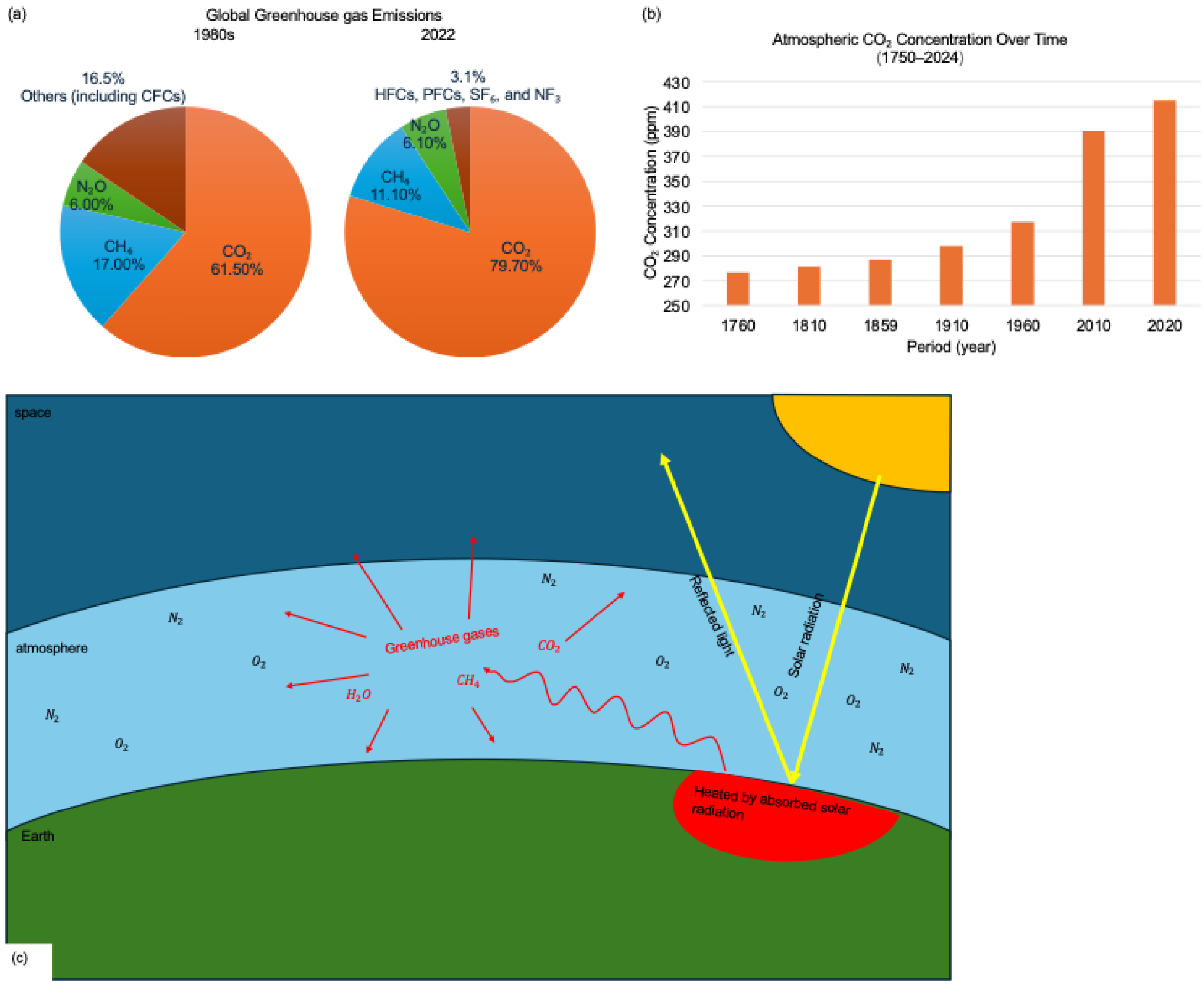


Figure 1. Increase of CO_2 after the Industrial Revolution. (a) The comparison of global greenhouse gas concentrations is shown between the 1980s and 2022. In the 1980s, CO_2 accounted for about 65% of total global greenhouse gas emissions, but in 2022, its share had increased to over 75% [1], [2]. (b) The actual amount of CO_2 continued to increase since the start of the Industrial Revolution in 1750, with a rapid increase between 1960 and 2010 [3], [4]. (c) The graphical scheme for the greenhouse effect. Greenhouse gases, including H_2O, CH_4, CO_2, etc., are atmospheric gases that absorb and emit infrared radiation particularly well, thereby significantly contributing to global warming [5]. (adopted from Schmidt et al., (2010))

Among the several technologies aimed at reducing excess atmospheric CO_2, the post-combustion method is the most well-suited and efficient way to capture and process industrial emissions, given its high compatibility with existing processes. Capture is accomplished by separating and capturing the CO_2 emitted with flue gas from industrial plants. The post-combustion method can also be adapted to the existing plant without changing the basic operating procedure (Figure 2) [6].

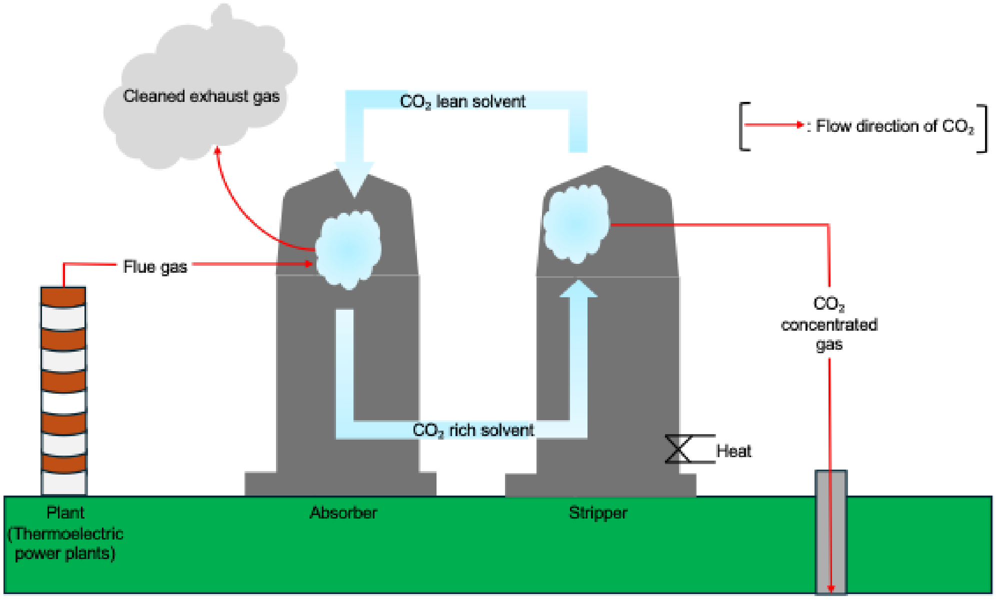
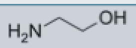


Figure 2. Structure of post-combustion system. The graphical scheme of the post-combustion system [6] (adopted from Ros et al., (2025)). When the flue gas initially enters the absorber, it reacts with the amine-based solvent, capturing carbon dioxide (CO_2). The CO_2-depleted gas is then released into the atmosphere. Then, the CO_2-retained solvent is transported to the Stripper, and heat treatment allows the rich solvent to separate into two substances: concentrated (or highly purified) CO_2 gas and CO_2-lean solvent.

The post-combustion strategy combines an absorber with a stripper. The absorber is designed to capture CO_2 from the plant's flue gas using an amine-based solvent, and the stripper is designed to re-emit CO_2 from the CO_2-rich solvent in a highly purified state, allowing it to be used as a source of future energy resources. The post-combustion method can minimize additional equipment costs and construction time, as it does not require altering the fundamental structure. Additionally, since this system can operate independently of the combustion process that forms flue gas, post-combustion methods have been receiving increasing attention for decarbonizing thermoelectric power plants and industrial processes. Post-combustion methods use amine-based solvents, thanks to their high reactivity with CO_2 [7]. Table. 1 represents each amine-based solvent's structure, relative carbon capture efficiency, and brief descriptions of its properties. [8], [9], [10]

Table 1. Structure and categorization of MEA, MDEA, AMP, and PZ, based on functional groups [8], [9], [10]. The efficiency in carbon capture varies with the concentration of each solvent, the amine circulation rate (cubic meters/hour), and, in many cases, the mixing and utilization of the solvents.

Amine-based solvent	Structure	Comparative carbon capture efficiency	Properties/Mechanism
MEA		High	Rapid absorption rate and high solubility Form carbamate/bicarbonate
MDEA		low	Tertiary amine, Form bicarbonate, Slow absorption rate. Rare to use it alone
AMP		Medium	Primary amine, Form carbamate, excellent in terms of thermal stability/regeneration
PZ		Very high	Strong nucleophile, Form carbamate rapidly, Very fast reaction rate

Among others, MEA (Monoethanolamine) has been traditionally utilized as a primary amine-based solvent. According to Bottoms (1930), MEA was originally utilized for separating acidic gases (CO_2, SO_2, and H_2S) from gas mixtures [11]. It is a water-soluble aliphatic amino alcohol that reacts chemically with acidic gases at low temperature and releases them upon heating. It has been broadly adopted in the initial industrial field due to its relatively high reactivity with CO_2. MEA has been developed since the early industrial era, so it has sufficient technological maturity. However, the MEA simultaneously has distinct disadvantages due to its high corrosivity and requires high regeneration energy, approximately 3.6-4.2 GJ/t CO_2 [12], [13].

To address these problems, MDEA or mixtures of individual amines, such as AMP with PZ (CESAR-1), were developed [14]. One alternative, MDEA (Methyl diethanolamine), absorbs CO_2 via the bicarbonate pathway rather than carbamate formation. MDEA has high thermal stability and low regeneration energy requirements, but a slow CO_2 absorption rate. Therefore, it is rare for MDEA to be used alone. During initial plant commissioning, MDEA was chosen for its ability to remove H_2S and retain a portion of the CO_2 in the residue gas. Its greater selectivity for H_2S than for CO_2 can be helpful once H_2S is removed as an acidic gas, but to remove CO_2, it can only be captured via a bicarbonate pathway, which is a slow reaction and ultimately undesirable for its sole use in CO_2 capture [15]. Furthermore, in the presence of oxygen and metal cations, MDEA undergoes oxidative degradation, forming corrosive byproducts such as formate and peroxide.

Even single-component amine solvents, such as MEA and MDEA, still involve a trade-off between absorption performance and regeneration energy. As a result, many researchers have turned to blended amine systems, in which one amine complements the shortcomings of the other. To maximize performance in both processes, recent research has widely used a mixture of amines to compensate for each solvent's weaknesses by combining two amine-based solvents with complementary properties. One of the representative amines is the CESAR-1 solvent, or a mixture of AMP (2-amino-2-methyl-1-propanol) and PZ (piperazine).

According to Mertdağ et al. (2023), the reboiler duty, which is the amount of heat to regenerate CO_2 from solvent, of CESAR-1 is about 20% lower than MEA and 10-15% lower than MDEA/PZ, together with a low heat of absorption and reduced solvent circulation rate (L/G) [16].

Solvent circulation rate (L/G) is expressed as two factors: liquid and gas. In the CO_2 capture process, the solvent is circulated throughout the overall system, which consists of the absorber and stripper. When a certain amine solvent possesses a high CO_2 loading capacity, the whole system can circulate a smaller amount of liquid amine to capture the same amount of CO_2. As CESAR-1 has a high CO_2 loading efficiency, it requires less liquid solvent to circulate, thereby reducing the additional energy-consuming operations of pumps, heating, cooling, etc. Therefore, CESAR-1 delivers improved energy efficiency while maintaining CO_2 absorption capacity equal to or above that of other systems. According to the modeling result, CESAR-1 shows higher CO_2-rich loading. When the system absorbs 90% of CO_2 from flue gas, the AMP-PZ system needs approximately 2.7 GJ/t CO_2; on the other hand, the MDEA-PZ system needs a high energy requirement, 2.9 GJ/t CO_2, while regenerating the CO_2-rich solvent [17].

CESAR-1 has recently attracted attention as a replacement for the MEA due to its high energy efficiency and stable operation; however, it still has intrinsic limitations when NO_x is present in the flue gas, as NO_x promotes its degradation in the CESAR-1 system. In this context, x is restricted to 1 and 2 only.

Apart from NO_x influx into the system, the solvent can be degraded through two steps: thermal degradation and oxidation. NO_x, especially, affects this oxidation step, forming carcinogenic substances such as nitrosamines and nitramines even at low concentrations, 0.5 - 2.35 ppm [18].

Byproducts formed during the degradation steps have been reported to reduce overall carbon capture efficiency.

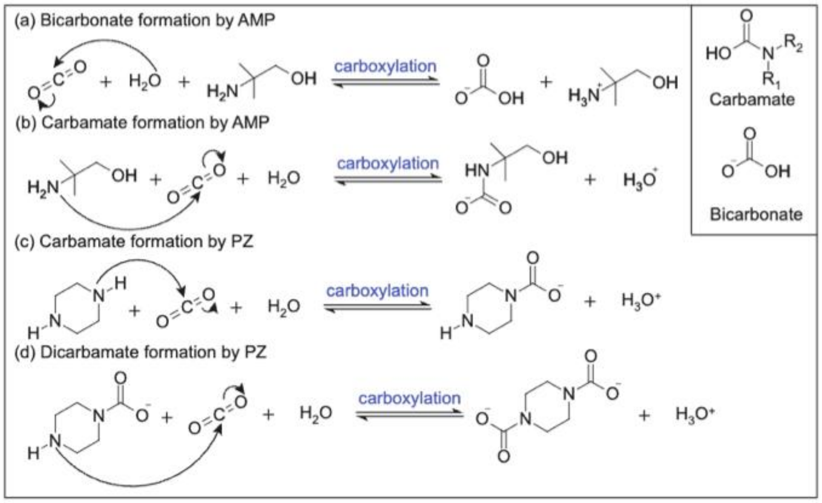
The Selective Catalytic Reduction (SCR) system is designed to resolve this issue and can utilize this flue gas, especially for NO_x. Engelhard Corporation first patented SCR technology in 1957, and since the early 1970s, SCRs have been widely used for both nitrogen oxide control from stationary combustion sources burning fossil fuels and for reducing solvent degradation in post-combustion carbon capture applications.

Taken together, CESAR-1 offers distinct advantages in energy efficiency compared to traditional MEA-based solvents; however, it also has critical drawbacks (nitrosamine/nitramine formation in a stripper process and solvent degradation), which serve as a barrier for utilization in industry sectors. This paper proposes a new flow design for the post-combustion carbon capture method, incorporating a SCR system upstream to prevent the formation of such carcinogenic substances in advance. As a review article, this paper focuses on the absorption and regeneration mechanism of CESAR-1, the degradation pathways under NO_x exposure, a SCR mechanism and associated catalyst, and proposes an integrated flow diagram of the overall process (SCR-CESAR system).

The Post-combustion Capture mechanism using CESAR-1

Mechanism in Absorber

In the CESAR-1 solvent system, CO_2 can be captured by amine species, which can be carboxylated to bicarbonate or carbamate, as shown in Figure 3.



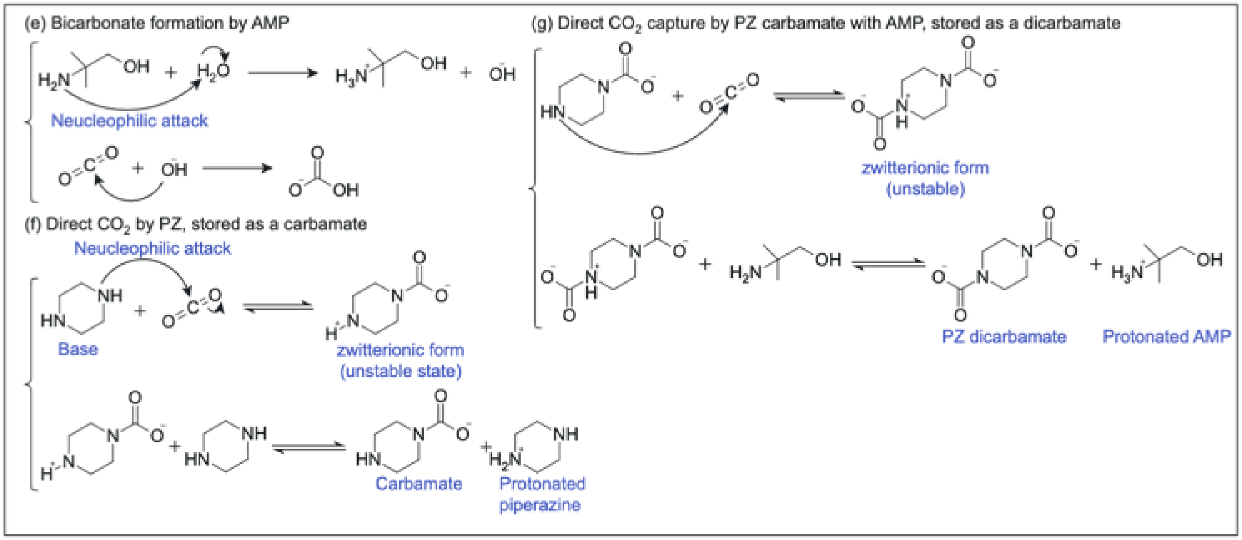


Figure 3. Carbon capture mechanism in the absorber. CO_2 is stored either in carbamate or bicarbonate form with an amine-based solvent. For (a) – (d), there are depicted brief results of the reaction mechanism in CESAR-1. Each reaction is conducted via carboxylation to capture CO_2 in the solvent. Even if AMP is still under the impression of steric hindrance by two methyl groups, a small amount of AMP-carbamate is present in stable form. For (e) – (g), more detailed processes of the reaction mechanism. Fundamental reactions involve nucleophilic attack of the lone electron pair of nitrogen on the electrophilic site, forming a protonated or zwitterionic form with charged ions [19], [20], [21].

The AMP (2-amino-2-methyl-1-propanol) and PZ (piperazine) blend acts cooperatively via two distinct mechanisms during the CO_2 capture process. AMP is mainly involved as a bicarbonate, whereas PZ tends to be reserved for the carbamate form.

For the pathway involving bicarbonate formation (Figure 3a), AMP is highly favored. The steric nature of both methyl substitutions ($-CH_3$) near the amine nitrogen accounts for the unfavorable nature of carbamate formation with AMP by hindering the approach of CO_2 near the Nitrogen atom. Therefore, AMP unfavorably reacts with the amine, but it does interact with water. Proton transfer equilibrium with water gives free hydroxide ions (OH^-), which attack dissolved carbon dioxide to form bicarbonate, as shown in Figure 3e [19], [20]. However, as seen in Figure 3b, the AMP-carbamate formation process is undeniably present, and it is as stable as MEA-carbamate due to a similar hydrolysis barrier, which prevents the carbamate from easily breaking apart. Nevertheless, AMP-carbamates are unlikely to be observed in the CESAR-1 system due to the kinetic preference in the bicarbonate pathway [20]. The methyl groups increase the negative charge density and polarizability of a nitrogen atom. They stabilize the binding of the hydrogen atoms in the amine group and the oxygen atom of the interaction between H_2O and AMP and destabilize the binding of CO_2. The charge redistribution also stabilizes the binding of the nitrogen atom of AMP with the surrounding H_2O molecules and makes CO_2 less accessible to the nitrogen site of the amine. Thus, the AMP-carbamate is less favorable than hydrated bicarbonate. [20]

Piperazine (PZ) reacts directly with CO_2 to form carbamate and dicarbamate species (Figures 3c–d and 3f-g). Given that there are two secondary amine centers on PZ, these nucleophilic sites react readily with CO_2, forming both carbamate and dicarbamate. This allows it to form a zwitterionic intermediate (a neutral species with both positive and negative charges), which is rapidly deprotonated to form piperazine carbamate (Figure 3f) [21]. The second amine site binds a CO_2 molecule, forming a dicarbamate (Figure 3g). These reactions indicate the direct CO_2 capture pathway, which proceeds via carboxylation and deprotonation.

Overall, the AMP/PZ combination shows a synergistic effect in CESAR-1. In particular, while AMP ensures a low energy conversion of CO_2 into bicarbonate via water-assisted hydrolysis, PZ guarantees rapid carbamate formation via direct carboxylation, improving the solvent's absorption kinetics, stability, and reducing the regeneration energy compared to conventional MEA-based solutions.

Mechanism in Stripper and degradation process

The staple regeneration mechanism is shown in the Figure 4.

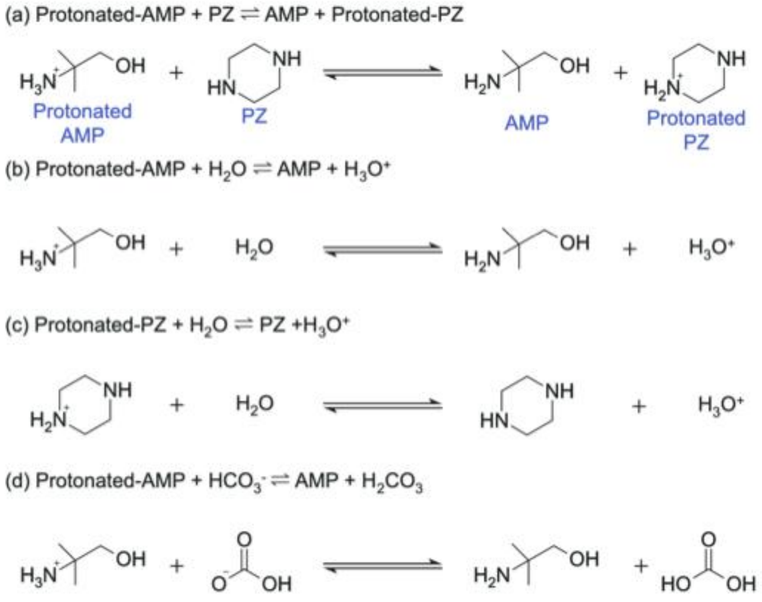


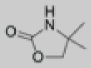
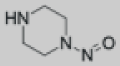
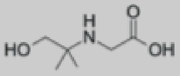
Figure 4. Regeneration mechanism in the stripper. Regeneration mechanism of each amine-based solvent (adapted from Li et al. (2023)) is described [22].

CO_2 is detached from the CO_2-rich solvent by infusing a certain range of heat into the stripper phase. This process, called regeneration, is the reverse of an absorption mechanism that restores contained CO_2 as bicarbonate in AMP and carbamate in PZ. Unlike the single-amine mechanism, the blended amine has multiple proton-transfer pathways to regenerate the original amine and produce CO_2. Furthermore, the presence of bicarbonate, which serves as a proton transfer path, is responsible for less regeneration energy than the independent use of each amine, according to Li et. al. (2023) [22]. Through these regeneration pathways, the recovered amines are transferred to the absorber and continuously undergo the same process until their life span is over.

Although the operating temperature and pressure generally vary depending on the operating conditions, the absorber operates under mild conditions around 40 ℃, 1.1 bar, where CESAR solvent can stably perform, and the stripper operates under relatively harsh conditions around 120-125 °C, 0.9 bar, which facilitates CESAR solvent regeneration [23], [24]. Since the CESAR-1 system operates over a wide temperature range and in the presence of oxygen-containing substances in the flue gas, it inevitably exhibits side effects, such as thermal degradation or oxidation, under these conditions.

The major byproducts derived from both thermal degradation and oxidation are depicted in Table 2.

Table 2. Chemical structures of byproducts generated from AMP, PZ, and AMP/PZ mixed solvent systems. The byproducts are formed during the regeneration process, in which CESAR-1 solvent unintentionally degrades into a few byproducts, taken from Buvik et al (2025) [25]. Interestingly, some degradation products do not form when AMP or PZ degrades individually but become prominent only when the two amines are mixed.

	Byproducts from AMP (Primary amine)	**Biproducts from PZ (Secondary amine)**	**New Biproducts from CESAR-1 (AMP/PZ)**
structure	 4,4-dimethyl-2-oxazolidinone (DMOZD) NH_3 Ammonia  2,4-lutidine (LUT)  2-[(2-amino-2-methylpropyl)amino]-2-methyl-1-propanol (AMP-AMP)	 N-formylpiperazine (FPZ) NH_3 Ammonia  Formic acid (FAc)  N-nitrosopiperazine (MNPZ)  Ethylenediamine (EDA)	 α,α−dimethyl−1−piperazineethanamine (DM-PZEA)  N-(2hydroxy-1,1-dimethylethyl)-glycine (HMeGly)

For the byproducts formed during the thermal degradation and oxidation of CESAR-1, the likelihood of returning from the CO_2-rich solvent to the lean solvent is low, which in turn reduces the CO_2 absorption capacity. Also, some organic acids, such as formic acid, acetic acid, and acetone, have been identified as major oxidation products at higher CO_2 loadings. A large amount of corrosion has been reported due to such acids produced by degradation, causing material damage and leading to equipment failure. These drawbacks from inherent thermal degradation and oxidation can serve a pivotal role in further usage of CESAR-1 in the Post-combustion carbon capture system. Researchers suggested maintaining the temperature in the stripper within a certain range of approximately 120 °C [24].

However, the presence of NO_2 in the stripper, which reacts to form N-nitrosopiperazine (MNPZ), poses a major problem due to its negative effects on the environment and humans. Specifically, increasing the risk of liver, lung, and gastrointestinal cancers upon prolonged exposure to MNPZ, and contaminating aqueous environments, was reported in Vikram et al. (2024) [26]. Furthermore, in mixtures rich in PZ, re-arrangement and hydrolysis of carbamate intermediates produce MNPZ and related nitrosamines even in the presence of low concentrations of NO_2 (30-50 ppm). These unexpected byproducts not only lead to solvent loss in the regeneration process, but also hazardous effects within or near the post carbon capture system. These impacts cannot be reduced or regulated by changing the reaction conditions, such as temperature or pressure [26]. Consequently, limiting NO_x concentrations is critical to minimize solvent loss and the associated environmental impact.

Selective Catalytic Reduction (SCR)

In SCR, NO_x is converted into harmless N_2 and H_2O with a reductant (traditionally, ammonia) by reaction on a supported catalyst's surface. The catalyst structure can reduce the associated activation energy and steer the reaction toward the N-N coupling pathway, minimizing the formation of undesired byproducts, such as NH_3 or N_2O, especially N_2O, which is considered a more potent greenhouse gas than CO_2.

In post-combustion CO_2 capture, the upstream SCR reduces the amount of NO_x entering the absorber/stripper loop, thereby reducing nitrosamines and oxidatively degrading the solvent. In general, ammonia-based SCR follows the reactions shown in Figure 5 [27].

(a) Similar concentration of NO, NO_2 (Fast SCR)

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

(b) NO dominant (Standard SCR)

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

(c) NO_2 dominant

$$6NO_2 + 9NH_3 \rightarrow 7N_2 + 12H_2O$$

Figure 5. Ammonia based SCR reaction mechanism. This set of reactions was taken from Iwasaki et al. (2010) [27] (a), Mechanism of fast SCR reaction. Fast SCR reaction becomes dominant when NO and NO_2 is at similar concentration (b), Mechanism of standard SCR reaction. Standard SCR reaction occurs when NO is dominant among NO_x substances (c), Mechanism of NO_2-dominant SCR reaction.

Based on the flue gas concentration, the tendency among the three reactions varied. According to Saito, Fujiwara (2023), the key factors in forming NO_x in a fossil fuel power plant are classified into Steam Flow Rate, Furnace Pressure, Combustion Air Temperature, and Steam Temperature near the furnace wall [28]. These factors function with either a positive or negative tendency to form NO_x. Based on these factors, the NO_x production mechanism is classified into Thermal NO_x, Fuel NO_x, and Prompt NO_x, as shown in the Figure. 6. Thermal NO_x occurred regardless of the presence of fuel and underwent a chain reaction rather than a direct reaction to form nitric oxide, because the boiler's temperature was not high enough for N-N bonding to be easily broken. On the other hand, Fuel NO_x results from the reaction of nitrogen-containing fuels with radicals, such as hydroxyl radical, oxygen radical, and hydrogen radical. At first, the nitrogen-containing fuel, in this case, ammonia, breaks one of its N-H bonds to form the NH_2 radical. This radical can help form NO by being oxidized by oxygen gas, an oxygen radical, or nitroxyl (HNO). Both Thermal NO_x and Fuel NO_x involve flame radicals, which facilitate the reactions. Prompt NO_x reaction mechanism is not considered significant, as the research stated that prompt NO_x can be negligible in the conventional combustion of pulverized coal [29], [30].

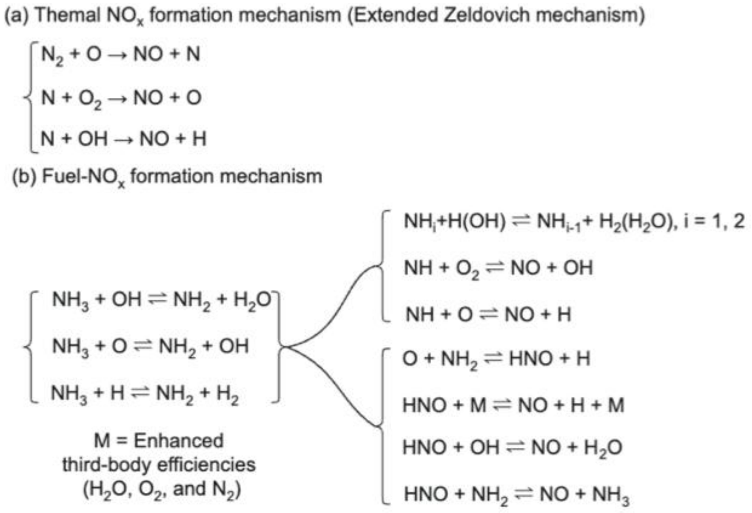


Figure 6. NO_x formation mechanism in power plants. There are two factors involving in NO_x formation. (a), Thermal NO_x formation occurs due to the high-temperature environment in the furnace/boiler [29]. (b), Fuel- NO_x formation comes from the nitrogen-containing species. In this case, ammonia was considered as the fuel [30].

Therefore, NO is accounted for the major portion of NO_x, while NO_2 accounts for below 10% of the total concentration. Thus, the Standard SCR reaction mechanism is the dominant process among the three SCR reaction mechanisms.

According to Kiani et al. (2024), evidence indicates that Standard SCR is best described by the Langmuir-Hinshelwood (L-H) mechanism, which is a process in which both reactants (and/or their activated species) are pre-chemically adsorbed on the catalyst before the reaction occurs. Unlike the L-H mechanism, both the Langmuir-Rideal (L-R) mechanism and the Eley-Rideal (E-R) mechanism are reactions where one chemisorbed species reacts with non-chemisorbed species. The difference between L-R and E-R mechanisms is how such non-chemisorbed species react with chemisorbed species. In the L-R mechanism, the gas-phase species directly collides with the chemisorbed species to initiate the reaction. On the other hand, for the E-R mechanism, the physisorbed species, which are usually formed by van der Waals bonding with the catalyst surface, indirectly react with the chemisorbed species, as shown in the Figure. 7 [31].

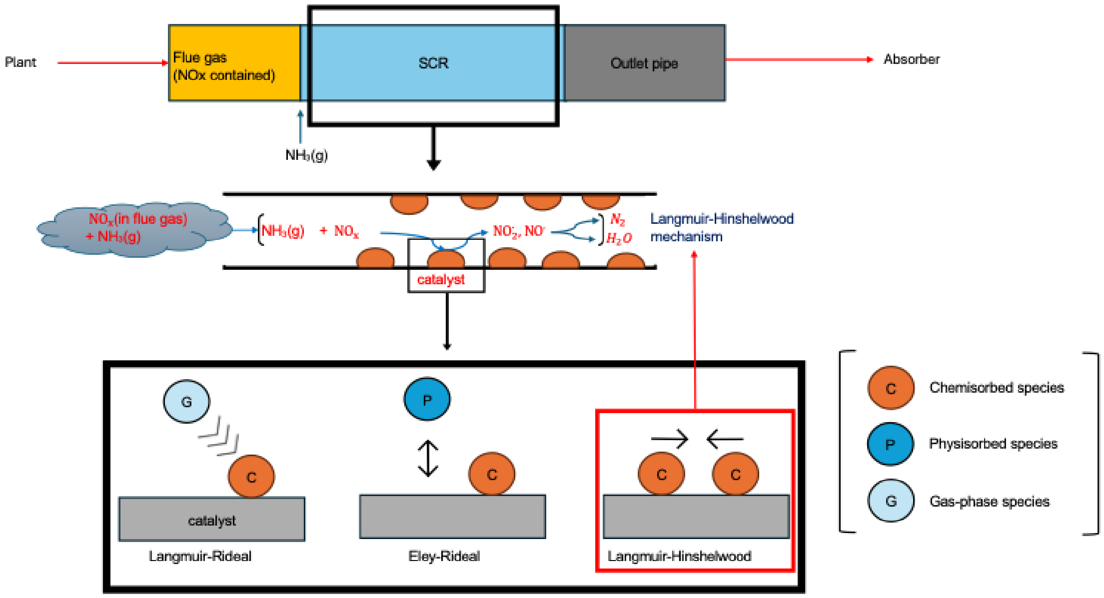


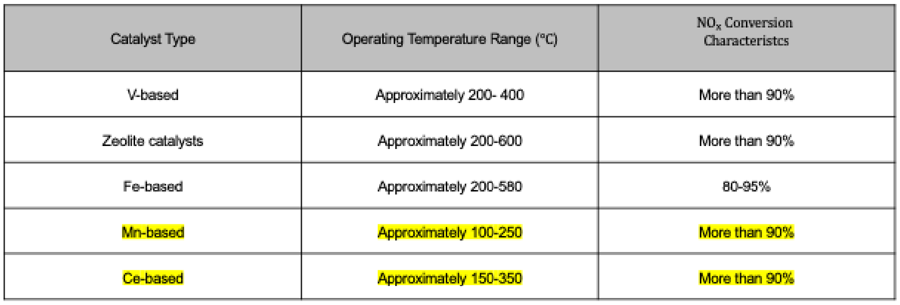
Figure 7. SCR system and its catalytic mechanism. In traditional ammonia-based SCR, ammonia gas is added to the flue gas before it enters the SCR system. Among three different catalytic mechanisms, ammonia SCR is known to follow the Langmuir-Hinshelwood (L-H) mechanism based on spectroscopic evidence and kinetic results. The graphical scheme of those catalysts' mechanisms was extracted from the 2024 work by Kiani and Wachs [31].

In addition, Kiani stated that the L-H mechanism accounts for higher reaction rates due to its secondary dependence on site density, whereas the E-R and L-R mechanisms typically exhibit first-order dependencies and are less commonly dominant pathways [31].

Specifically, the L-H mechanism's second-order dependence on catalytic site density was confirmed by spectroscopic evidence for the presence of surface intermediate species such as NH_2NO. Even though non-idealities, such as site heterogeneity and adsorbate-adsorbate interactions, can seemingly indicate that the kinetic is followed by the E-R mechanism, the L-H mechanism is accepted as the primary route for the ammonia-based SCR. That is the main reason why so many researchers are conducting research to maximize active-site exposure and increase geometric surface area to enhance overall catalytic performance. This could be achieved by considering catalyst structure, such as microstructure, pore texture, and surface area [32].

Regarding catalyst type, the activation temperature of each catalyst is an important consideration for maximizing overall system energy efficiency. According to Table 2, the traditionally used and prevalent catalyst is a Vanadium (V)-based catalyst, which is only useful for power plants that emit high-temperature flue gas [33].

Table 2. Summary of operating conditions for each catalyst. Taken from Wei et al. (2024), ultra-low-temperature SCR catalysts, such as Mn-based and Ce-based catalysts, are suitable for fossil fuel power plants due to their lower operating temperatures compared with conventional V-based, Zeolite, and Fe-based catalysts.



Catalyst Type	Operating Temperature Range (℃)	NO_x Conversion Characteristcs
V-based	Approximately 200- 400	More than 90%
Zeolite catalysts	Approximately 200-600	More than 90%
Fe-based	Approximately 200-580	80-95%
Mn-based	Approximately 100-250	More than 90%
Ce-based	Approximately 150-350	More than 90%

However, such V-based catalysts' operating temperature range doesn't fit well with municipal waste incineration power plants, which usually emit flue gas at around 100-200 ℃. Ultra-low-temperature SCR catalysts, such as Mn-based and Ce-based catalysts, are suitable for use in these types of power plants. Therefore, catalysts should be selected based on the types of plants.

Suggestion of revised Post Carbon Capture system, integrating CESAR-1 with SCR

The distinct advantage of the CESAR-1 is its ability to effectively eliminate CO_2 from flue gas. However, as mentioned in Section 2.2, even a small amount of NO_x in the flue gas can facilitate degradation in the stripper, forming carcinogenic substances, which in turn form additional byproducts that serve as a foundation for further degradation. To minimize this effect, this proposal suggests a revised CESAR-1 system with the SCR method, hereafter referred to as a SCR-CESAR-1 system. (Figure 8.) To briefly introduce our system, flue gas, which typically contains 120,000-150,000 ppm CO_2 and 158 ppm NO_x, is heated to 150℃ - 250 ℃ in the heater. [34], [35] To undergo reaction at low temperature effectively, the catalyst should be chosen among the Ultra-low-temperature SCR catalysts [33]. After NO_x is removed, flue gas is cooled to the absorber's operating temperature (around 40℃) via a heat exchanger and then is introduced into the absorber. The measured temperature of flue gas from coal-fired power plants is around 100-150 ℃. To react NO_x effectively with the catalyst in the SCR Reactor, the heater should be adjusted before the flue gas enters the SCR reactor to deliver a specific amount of energy for reaction. To undergo reaction at low temperatures effectively, the catalyst should be chosen from Ultra-low-temperature SCR catalysts. Once the NO_x is removed from the flue gas, leaving nitrogen gas and water, it should be cooled to the absorber's operating temperature via a heat exchanger, and then the treated flue gas is introduced into the absorber. CO_2 is absorbed with the CESAR-1 solvent to form carbamate, bicarbonate, Protonated-AMP, and Protonated-PZ. CO_2-free gas (clean gas) is emitted to the atmosphere, while CO_2-rich solvent is transported to the stripper for regeneration. During the regeneration process, the CO_2-rich CESAR-1 solvent, in the form of carbamate, bicarbonate, and each protonated amine, is heated with an electrical heater to release CO_2 from the solvent. The detached solvent is captured and returned to the absorber until the solvent's life span is over, and the generated CO_2 is stored in the CO_2 container.

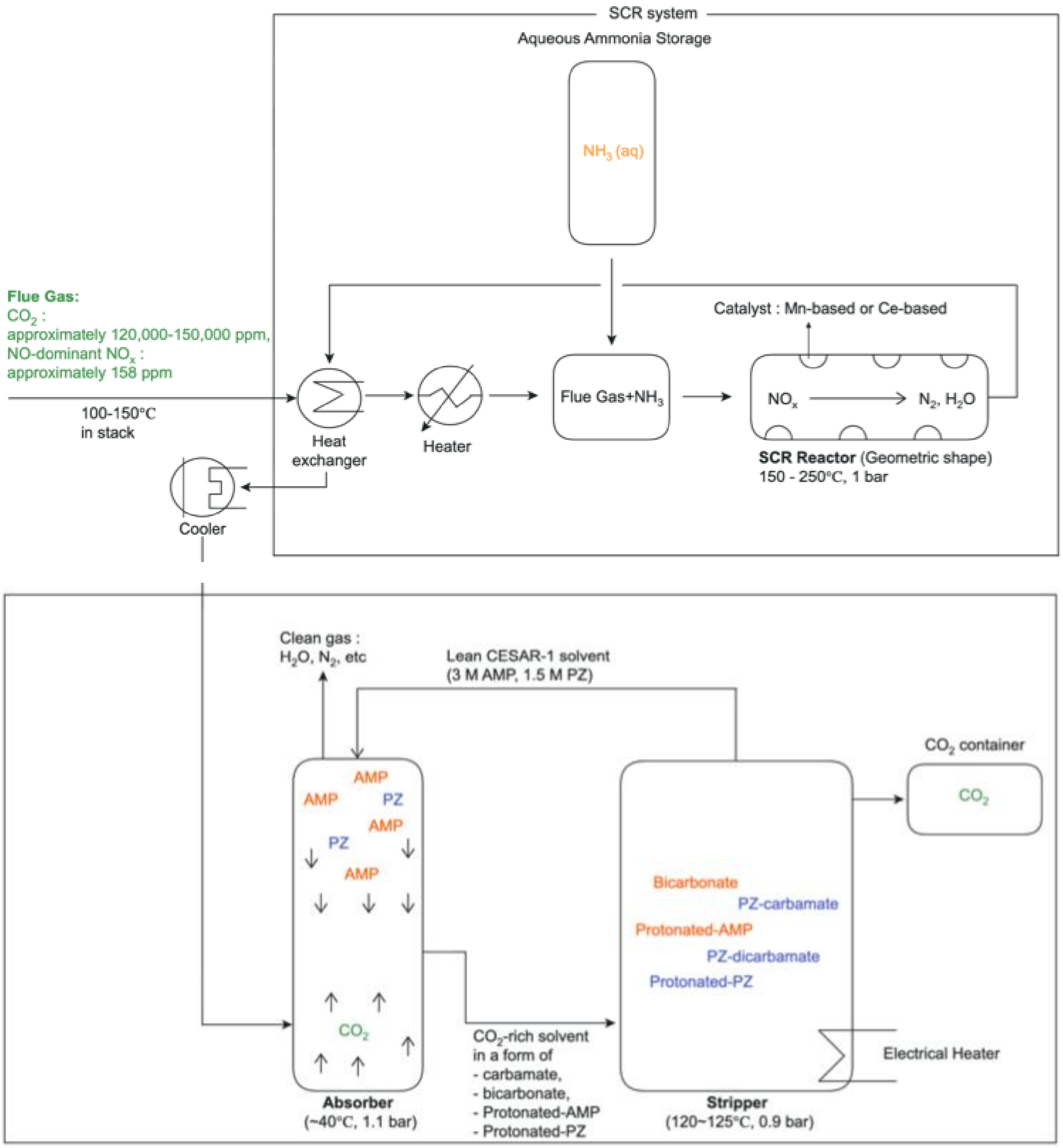


Figure. 8. SCR-CESAR system flow diagram. Flue gas containing CO_2 and NO_x goes into the SCR system. Within the system, a significant amount of NO_x is converted to N_2 and H_2O within the SCR reactor. The remaining gas, which contains non-disrupted CO_2 is cooled and enters the absorber to proceed post-combustion carbon capture process. CO_2 is captured and stored in a container after this reaction.

This combined system (SCR-CESAR system) has several advantages.

First, the SCR–CESAR system is achieved by maintaining similar operating temperatures throughout the entire process—from the thermoelectric power plant to the ammonia-based SCR unit and finally to the CESAR-1 absorber & stripper—while minimizing the effort required for wide temperature changes. This is especially achieved by the usage of ultra-low-temperature SCR catalysts in the design.

Second, the use of Mn-based catalysts not only saves the required energy but also reduces toxicity compared with V-based catalysts, thereby contributing to green chemistry and sustainable industrial processes. [36] Furthermore, the Mn-based catalyst reported that it can be activated in less toxic solvents - such as oxygen molecules and hydrogen peroxide – in which the water is produced as a byproduct, which is also an environmentally friendly substance.

Finally, even though not all the injected ammonia for SCR operation is fully utilized and some remains as ammonia slip, the introduction of an ammonia slip catalyst (ASC) at the end of the SCR system enables the remaining ammonia to react with NO_x. This reduces the need for additional ammonia injection, thereby lowering the overall ammonia consumption and associated costs [37].

Conclusion

Since CO_2 is the greenhouse gas largely produced by human activity, measures to limit these emissions have often been described as an environmental imperative. Among the different types of carbon capture processes, post-combustion capture is widely used, as it can be retrofitted into existing industrial plants and processes. Amine-based absorption using CESAR-1, a blended (AMP) / (PZ) solvent widely applied in post-combustion CO_2 capture, has gained attention due to its higher CO_2 loading capacity and lower regeneration energy, since each amine compensates for the other’s weakness.

However, since CO_2 is not the sole constituent of the flue gas, the presence of other constituents, especially NO_x (where x is mostly 1 or 2), in post-combustion CO_2 capture also poses potential problems, including (1) generation of MNPZ, a harmful byproduct to human health and the surrounding aqueous environment, and (2) solvent loss during regeneration. This can be addressed by installing an SCR system upstream of the CESAR-1 process to remove NO_x from the flue stream before it passes through the CESAR-1 absorber. The SCR-CESAR-1 combined system includes the SCR reactor, CO_2 absorber, and stripper that comprises the CESAR-1. The system's advantages include a similar reaction temperature across all stages, which limits heat losses from heating and cooling. The proposed system also uses manganese-based ultra-low-temperature catalysts in the SCR, which are considered less harmful than prevalent yet toxic catalysts such as vanadium.

Additionally, an Ammonia Slip Catalyst (ASC) system can be used to consume unreacted ammonia that may remain after the SCR reaction, thereby reducing the amount of ammonia that must be injected into the flue gas, saving costs and reducing emissions.

For a process or plant with (1) a large NO_x emission, (2) ammonia in the flue gas and (3) temperature of the flue gas within a certain range of 100-200 °C, such as a thermoelectric power plant and a chemical plant, the SCR-CESAR-1 system is particularly suitable. This combined system enables cost-effective, environmentally friendly reaction mechanism for NO_x and CO_2 emission reduction.

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References

[1] Intergovernmental Panel on Climate Change (IPCC). Climate Change: The IPCC 1990 and 1992 Assessments; Overview and Policymaker Summaries and 1992 IPCC Supplement; World Meteorological Organization: Geneva, Switzerland; United Nations Environment Programme: Nairobi, Kenya, 1992; ISBN 0-662-19821-2.

[2] López, J. C.; Quijano, G.; Souza, T. S. O.; Estrada, J. M.; Lebrero, R.; Muñoz, R. Biotechnologies for Greenhouse Gases (CH_4, N_2O, and CO_2) Abatement: State of the Art and Challenges. Appl. Microbiol. Biotechnol. 2013, 97 (6), 2277–2303. https://doi.org/10.1007/s00253-013-4734-z.

[3] Means of Scripps Institution of Oceanography Continuous Data at Mauna Loa and South Pole provided by KenMaarie (personal communication) NASA Goddard Institute for Space Studies (GISS). Global Mean CO_2 Mixing Ratios (ppm): Observations and Future Scenarios. NASA GISS Climate Data; https://data.giss.nasa.gov/modelforce/ghgases/Fig1A.ext.txt

[4] NOAA Global Monitoring Laboratory. Trends in CO2, NOAA, 2024 https://gml.noaa.gov/webdata/ccgg/trends/co2/co2_mm_mlo.txt.

[5] Schmidt, G. A.; Ruedy, R.; Miller, R. L.; Lacis, A. A. Attribution of the Present-Day Total Greenhouse Effect. J. Geophys. Res. Atmos. 2010, 115(D20), D20106. https://doi.org/10.1029/2010JD014287

[6] Ros, J.; Agon, N.; Louwagie, D.; Gutiérrez-Sanchez, O.; Huizinga, A.; Gravesteijn, P.; Kruijne, M.; Skylogianni, E.; van Os, P.; Monteiro, J. G. M.CESAR1 Carbon Capture Pilot Campaigns at an Industrial Metal Recycling Site and Analysis of Solvent Degradation Behavior.Ind. Eng. Chem. Res. 2025, 64(10), 5548–5565.https://doi.org/10.1021/acs.iecr.4c03998

[7] Lv, B.; Guo, B.; Zhou, Z.; Jing, G. Mechanisms of CO_2 Capture into Monoethanolamine Solution with Different CO_2 Loading during the Absorption/Desorption Processes. Environ. Sci. Technol. 2015, 49 (17), 10728–10735. https://doi.org/10.1021/acs.est.5b02356

[8] Zhang, Z.; Vo, D.-N.; Kum, J.; Hong, S.-H.; Lee, C.-H. Enhancing Energy Efficiency of Chemical Absorption-Based CO_2 Capture Process with Advanced Waste-Heat Recovery Modules at a High Capture Rate. Chem. Eng. J. 2023, 472, 144918. https://doi.org/10.1016/j.cej.2023.144918.

[9] Wang, N.; Wang, D.; Krook-Riekkola, A.; Ji, X. MEA-Based CO_2 Capture: A Study Focuses on MEA Concentrations and Process Parameters. Front. Energy Res. 2023, 11, 1230743. https://doi.org/10.3389/fenrg.2023.1230743.

[10] Hasan, S.; Abbas, A. J.; Nasr, G. G. Improving the Carbon Capture Efficiency for Gas Power Plants through Amine-Based Absorbents. Sustainability 2021, 13 (1), 72. https://doi.org/10.3390/su13010072

[11] Bottoms, R. R. Process for Separating Acidic Gases. U.S. Patent 1,783,901, Dec 2, 1930.

[12] Vinjarapu, S. H. B.; Neerup, R.; Larsen, A. H.; Jørsboe, J. K.; Villadsen, S. N. B.; Jensen, S.; Karlsson, J. L.; Kappel, J.; Lassen, H.; Blinksbjerg, P.; von Solms, N.; Fosbøl, P. L.

Results from Pilot-Scale CO_2 Capture Testing Using 30 wt % MEA at a Waste-to-Energy Facility: Optimisation through Parametric Analysis. Appl. Energy 2024, 355, 122193. https://doi.org/10.1016/j.apenergy.2023.122193.

[13] Zhang, W.; Liu, H.; Sun, C.; Cakstins, J.; Sun, C.; Snape, C. E. Parametric Study on the Regeneration Heat Requirement of an Amine-Based Solid Adsorbent Process for Post-Combustion Carbon Capture. Appl. Energy 2016, 168, 394–405. https://doi.org/10.1016/j.apenergy.2016.01.049.

[14] Haimour, N.; Sandall, O. C. Absorption of Carbon Dioxide into Aqueous Methyldiethanolamine. Chem. Eng. Sci. 1984, 39 (12), 1791–1796. https://doi.org/10.1016/0009-2509(84)80115-3.

[15] Mackenzie, D. H.; Prambil, F. C.; Daniels, C. A.; Bullin, J. A. Design and Operation of a Selective Sweetening Plant Using MDEA. Energy Progress 1987, 7 (1), 31–36.

[16] Mertdag, Y. Process Simulation and Techno-Economic Analysis of CESAR-1 Solvent in Post Combustion Carbon Capture, and Benchmarking with MEA Solvent; Master Thesis, Aalborg University, 2023.

[17] Smahi, A.; Kanniche, M.; Bouallou, C.; Jourdan, N.; Authier, O. CO_2 Capture in MDEA–PZ and AMP–PZ Solvents: ELECNRTL vs ENRTL-RK Models and Their Efficiency in Natural Gas Combined Cycles. Proc. 17th Int. Conf. on Greenhouse Gas Control Technologies (GHGT-17), Calgary, Canada, Oct 20–24, 2024. Available at SSRN: https://ssrn.com/abstract=5025846

[18] Ros, J.; Agon, N.; Louwagie, D.; Gutiérrez-Sanchez, O.; Huizinga, A.; Gravesteijn, P.; Kruijne, M.; Skylogianni, E.; van Os, P.; Moretz-Sohn Monteiro, J. G. M. CESAR1 Carbon Capture Pilot Campaigns at an Industrial Metal Recycling Site and Analysis of Solvent Degradation Behavior. Ind. Eng. Chem. Res. 2025, 64 (10), 5548–5565. https://doi.org/10.1021/acs.iecr.4c03998

[19] Morgan, J. C.; Campbell, M.; Putta, K. R.; Shah, M. I.; Matuszewski, M.; Omell, B. Development of Process Model of CESAR1 Solvent System and Validation with Large Pilot Data. Presented at the 16th International Conference on Greenhouse Gas Control Technologies (GHGT-16), Lyon, France, October 23–27, 2022.

[20] Stowe, H. M.; Vilčiauskas, L.; Paek, E.; Hwang, G. S. On the Origin of Preferred Bicarbonate Production from Carbon Dioxide (CO_2) Capture in Aqueous 2-Amino-2-Methyl-1-Propanol (AMP). Phys. Chem. Chem. Phys. 2015, 17, 29184–29192. https://doi.org/10.1039/C5CP04876A.

[21] Conway, W.; Fernandes, D.; Beyad, Y.; Burns, R.; Lawrance, G.; Puxty, G.; Maeder, M. Reactions of CO_2 with Aqueous Piperazine Solutions: Formation and Decomposition of Mono- and Dicarbamic Acids/Carbamates of Piperazine at 25.0 °C. J. Phys. Chem. A 2013, 117, 806–813. https://doi.org/10.1021/jp310560b.

[22] Li, T.; Yu, Q.; Barzagli, F.; Li, C.; Che, M.; Zhang, Z.; Zhang, R. Energy Efficient Catalytic CO_2 Desorption: Mechanism, Technological Progress and Perspective. Carbon Capture Sci. Technol. 2023, 6, 100099. https://doi.org/10.1016/j.ccst.2023.100099

[23] Ros, J.; Agon, N.; Louwagie, D.; Gutiérrez-Sanchez, O.; Huizinga, A.; Gravesteijn, P.; Kruijne, M.; Skylogianni, E.; van Os, P.; Moretz-Sohn Monteiro, J. G. CESAR1 Carbon Capture Pilot Campaigns at an Industrial Metal Recycling Site and Analysis of Solvent Degradation Behavior. Ind. Eng. Chem. Res. 2025, 64, 5548-5565. https://doi.org/10.1021/acs.iecr.4c03998.

[24] Languille, B.; Drageset, A.; Mikoviny, T.; Zardin, E.; Benquet, C.; Ullestad, Ø.; Aronson, M.; Kleppe, E. R.; Wisthaler, A. Atmospheric emissions of amino-methyl-propanol, piperazine and their degradation products during the 2019-20 ALIGN-CCUS campaign at the Technology Centre Mongstad. Presented at the 15th International Conference on Greenhouse Gas Control Technologies (GHGT-15), Abu Dhabi, UAE, March 15–18, 2021.

[25] Buvik, V.; Vernstad, K.; Grimstvedt, A.; Høisæter, K. K.; Vevelstad, S. J.; Knuutila, H. K. Degradation of 2-Amino-2-Methylpropanol and Piperazine at CO_2 Capture-Relevant Conditions. Ind. Eng. Chem. Res. 2025, 64 (22), 11000–11020. https://doi.org/10.1021/acs.iecr.5c00527

[26] Vikram, H. P. R.; Kumar, T. P.; Kumar, G.; Deka, R.; Suhail, S. M.; Jat, S.; Bannimath, N.; Padmanabhan, G.; Chandan, R. S.; Kumar, P.; Gurupadayya, B. Nitrosamines Crisis in Pharmaceuticals—Insights on Toxicological Implications, Root Causes and Risk Assessment: A

Systematic Review. J. Pharm. Anal. 2024, 14 (5), 100919. https://doi.org/10.1016/j.jpha.2023.12.009.

[27] Iwasaki, M.; Shinjoh, H. A Comparative Study of “Standard”, “Fast” and “NO_2” SCR Reactions over Fe/Zeolite Catalyst. Appl. Catal. A: Gen. 2010, 390, 71–77. https://doi.org/10.1016/j.apcata.2010.09.034.

[28] Saito, T.; Fujiwara, K. Causal analysis of nitrogen oxides emissions process in coal-fired power plant with LiNGAM. Front. Anal. Sci. 2023, 3, 1045324. https://doi.org/10.3389/frans.2023.1045324

[29] Miller, J. A.; Bowman, C. T. Mechanisms of Nitrogen Oxide Formation in Combustion Processes. Combust. Flame 1989, 76, 1–31. https://doi.org/10.1016/0360-1285(89)90017-8

[30] Zevenhoven, R.; Kilpinen, P. NITROGEN — Mechanisms and Kinetics of Nitrogen Compounds in Combustion; Åbo Akademi University: Finland, 2002; Chapter 4.

[31] Kiani, D.; Wachs, I. E. Practical Considerations for Understanding Surface Reaction Mechanisms Involved in Heterogeneous Catalysis. ACS Catal. 2024, 14 (22), 16770–16784. https://doi.org/10.1021/acscatal.4c05188

[32] Trovarelli, A.; Llorca, J. Catalysis Today 1998, 39 (2), 141-153. https://doi.org/10.1016/S0920-5861(98)00050-9.

[33] Wei, F.; Rao, Y.; Huang, Y.; Wang, W.; Mei, H.; et al. The New Challenges for the Development of NH3-SCR Catalysts under New Situation of Energy Transition in Power Generation Industry. Chin. Chem. Lett. 2024, 35, 108931. https://doi.org/10.1016/j.cclet.2023.108931.

[34] Songolzadeh, M.; Soleimani, M.; Takht Ravanchi, M.; Songolzadeh, R. Carbon Dioxide Separation from Flue Gases: A Technological Review Emphasizing Reduction in Greenhouse Gas Emissions. The Scientific World Journal 2014, 2014, 828131. https://doi.org/10.1155/2014/828131

[35] Li, Z.; Fan, T. W.; Lun, M. S.; Li, Q. Optimization of Municipal Solid Waste Incineration for Low-NOx Emissions through Numerical Simulation. Sci. Rep. 2024, 14, 19309. https://doi.org/10.1038/s41598-024-69019-w.

[36] Kazemi, M.; Ali, R.; Jain, V.; Ballal, S.; Abosaoda, M. K.; Singh, A.; Krithiga, T.; Joshi, K. K.; Javahershenas, R. A Comprehensive Review on Magnetic Manganese as Catalysts in Organic Synthesis. RSC Adv. 2025, 15, 23054. https://doi.org/10.1039/d5ra02493e.

[37] Manassero, D.; Bonvicini, F.; Ravelli, D.; Malavasi, L.; Carnelli, L.; Arlotti, G.; Pellacani, G. Pure Ammonia-Fueled Roller Kiln for the Production of Ceramic Tiles: A First Demonstration. Energy Fuels 2024, 38 (7), 6355–6362. https://doi.org/10.1021/acs.energyfuels.4c03745.

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