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Effects of Composition, Structure of Amine, Pressure and Temperature on CO2 Capture Efficiency and Corrosion of Carbon Steels using Amine-Based Solvents: a Review

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The emission of carbon dioxide (CO2) into the atmosphere is a significant environmental problem. Many technologies are proposed and implemented to sequester CO2 before it is released into the atmosphere. For capturing carbon dioxide (CO2) from exhaust gas and syngas streams in all industrial processes and combustion, chemical absorption using amine-based solvents has shown to be the most studied, reliable, and efficient technology. As a result of the dissolution of CO2 gas and its reaction with the amine solvents, the solution becomes corrosive. This undesirable phenomenon creates a corrosion problem in the absorption column, usually carbon steel. This review paper aims to understand the effects of the variables amine composition in the solution, amine structure, pressure, and temperature on the efficiency of CO2 capture and corrosion of carbon steels using chemical absorption technology using amine-based solvents.

1. Introduction

The generation and emission of greenhouse gases represent a major global problem due to the negative environmental impact of greenhouse gases, such as global warming and climate change (Cao et al., 2021). 76 % of greenhouse gases (GHG) worldwide come from carbon dioxide (CO_2). Carbon dioxide emissions are now a severe global concern (Aghel et al., 2022). Carbon dioxide emissions into the atmosphere have reached a maximum of 36 billion tons per year (versus 6 billion tons in 1950). Global warming and climate change are primarily caused by the release of anthropogenic CO_2 during the combustion of conventional fossil fuels. It is projected that CO_2 emissions by 2035 will reach 37.2 gigatons if it is not adequately checked. As a result of this scenario, sea levels would rise, droughts, flooding, storms, severe heat waves, and other natural disasters would occur. A large number of industries emit large amounts of CO_2 to meet basic needs and requirements, such as the food processing industry, cement industry, aluminum industry, iron and steel industry, petrochemical industry, thermal power plant, and numerous other chemically-based industries (Gautam and Mondal, 2023). There are two main types of CO_2 emissions: combustion emissions and process emissions. The combustion of conventional fossil fuels such as coal, natural gas, and oil releases enormous amounts of CO_2 (Dash et al., 2022).

Similarly, all other CO_2 emissions other than those from combustion processes are classified as process emissions. As a result of chemical reactions, limestone is converted into lime, iron ore is converted into iron metal, and water is shifted, all of which emit CO_2 into the atmosphere. In some industrial units, combustion and process emissions are combined before being treated for high-purity CO_2 (Gautam and Mondal, 2023). To comply with the Paris Agreement, net greenhouse gas emissions must be zero or negative by 2050 to keep global warming below 1.5 – 2 ºC compared to pre-industrial levels (Fernandez, 2022).

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The world community faces two opposing challenges: increasing global energy consumption that allows energy security and mitigating climate change (Helei et al., 2021). In this way, countries are currently focusing on implementing CO_2 capture and sequestration technologies to comply with environmental regulations and slow global warming.

CO_2 capture using amines has become a popular technology due to the advantages of chemical absorption and the fact that it is a cyclic process. Amine-based solvents for post-combustion CO_2 capture have the benefit of directly removing CO_2 from flue gas. There are three types of amines. Primary amines are very reactive, but have low absorption capacities. Secondary amines are less reactive than primary amines. Compared with tertiary amines, tertiary amines have a low reactivity and a high absorption rate (Mailhol and Bouallou, 2021).

Additionally, the method is comparatively inexpensive and easily adaptable to existing applications (Aghel et al., 2022). Generally, CO_2 is not very corrosive to materials in itself, but when it dissolves in water or when it dissolves in CO_2, it increases its corrosive characteristics, resulting in high corrosion rates (Pérez, 2013).

According to industry estimates, 80 % of accidents that occur during pipeline operation are caused by corrosion, primarily due to the continued use of ferrous metals that are not adequately protected. It is imperative to minimize equipment deterioration, as this usually results in prolonged downtime and unnecessary costs (Shamsa et al., 2021). Unfortunately, aqueous amine absorbents can corrode equipment, which is one of the main problems facing CO_2 capture technologies. Although amines can inhibit some corrosion processes, under CO_2 capture conditions, they can cause severe corrosion on carbon steel equipment due to the formation of bicarbonate and carbamate species (Li et al., 2020).

Carbon steel is a type of steel that has an approximate carbon percentage of 0.1 %–0.3 % and up to 2.1 % at most by weight. Carbon steels are categorized into low carbon steel, medium carbon steel, and high carbon steel based on the amount of carbon they contain. Carbon steel exhibits unique properties in which an increase in the carbon percentage would cause the ductility of the steel to decrease but the tensile strength and hardness to increase.

Due to its low price and high tensile strength, carbon steel is used to make most of the CO_2 absorbers. Unfortunately, the utilization of carbon steel as a building material (especially for PCCC technology) is limited by corrosion issues (Ooi et al., 2020).

The review of relevant information on the effects of four significant variables, composition, structure, pressure, and temperature, on the efficiency of CO_2 capture and corrosion of carbon steels using amine-based solvents is presented in this work. This research aims to reveal relevant information on these variables, the efficiency of CO_2 capture, and the corrosion impact of carbon steel since absorption columns are made from carbon steel in large part of the industrial processes.

2. CO_2 capture process using amines

Amine-based solvents have been found to have a good absorption capacity for CO_2 gas. Consequently, it is the most mature solvent in CO_2 absorption (Nwaoha et al., 2017). This technology offers capture with high efficiency (> 90 %) and selectivity (it is used in processes of separation and capture of CO_2 in different gas mixtures) and with lower energy consumption compared to other capture technologies (absorption physical, by membranes, calcination/carbonation cycle). In addition, it is a highly reversible process since a large amount of the amine used in the absorption process can be regenerated and used again.

Table 1 shows the Advantages and disadvantages of amine-based solvents. The capture process generates a solution, which can be corrosive, and this phenomenon is not desired at an industrial level. Among the most commercially used amines are monoethanolamine (MEA) due to its low cost, diethanolamine (DEA) and methyldiethanolamine (MDEA) are also used. Mixed amines or polyamines such as piperazine (PZ) and 4-amino-1-propyl-piperidine (4A1PPD) are currently employed, which presents as one of the main attributes, that they tend to have lower corrosion rates (Hernández, 2019).

The chemical absorption process using amines as solvents in a column is the best known and applied method for CO_2 capture. Where methyldiethanolamine (MDEA) stands out as a conventional solvent for CO_2 capture, it provides low fugitive emissions, in addition to the fact that the process has low regeneration heat and offers a high CO_2 absorption capacity (Shahid et al., 2021). In addition, it is the most suitable solvent for processing natural gas, which needs to remove CO_2, and such a process is carried out under high pressure and high concentrations of CO_2. Using primary and secondary amines produces a direct reaction with CO_2.

Table 1: Advantages and disadvantages of solvents (Aghel et al., 2022).

Types solvent	Disadvantages	Advantages
MEA (monoethanolamine)	• High vapour pressure • High corrosivity • High energy demand for regeneration	• High reactivity with CO_2 • Availability and low cost • High absorption rate
MDEA (methyldiethanolamine)	• Low rate of reaction with CO_2	• Low corrosivity • High resistance against degradation • Selective absorption of H_2S in the presence of CO_2 • Flexible
DEA (diethanolamine)	• Production of corrosive acids in the presence of O_2 • Unable to carry low-pressure gases	• Low corrosivity and foaming Lower energy demand
TEA (triethanolamine)	• Lower absorption rate compared to MEA	• Lower costs due to less energy demand
DIPA (bis(2-hydroxypropyl)amine)	• Weak CO_2 absorption	• Non-corrosive • Low vapour demand for recovery
PZ (piperazine)	• Limited concentration for usage	• High absorption capacity, about two times of MEA • Carbamate production when reacts with CO_2
AEEA (2-aminoethyl) ethanolamine)	• Solvent degradation	• High CO_2 absorption and cyclic absorption capacity. • Low energy demand for recovery.
AMP (2- amino-2-methyl-1-propanol)	• Lower amine-CO_2 mass transfer compared with MEA	• High CO_2 absorption and loading • Less corrosive

In the case of tertiary amines, there are stages before the reaction in the capture process (see Table 2). Both primary and secondary amines are weak bases that tend to react with CO2 to form carbamates (Ooi et al., 2020). This reaction is reversible; therefore, the amine solvent can be regenerated for subsequent absorption use.The chemical absorption process using amines as solvents in a column is the best known and applied method for CO_2 capture. Where methyldiethanolamine (MDEA) stands out as a conventional solvent for CO_2 capture, it provides low fugitive emissions, in addition to the fact that the process has low regeneration heat and offers a high CO_2 absorption capacity (Shahid et al., 2021). In addition, it is the most suitable solvent for processing natural gas, which needs to remove CO_2, and such a process is carried out under high pressure and high concentrations of CO_2. Using primary and secondary amines produces a direct reaction with CO_2. In the case of tertiary amines, there are stages before the reaction in the capture process (see Table 2). Both primary and secondary amines are weak bases that tend to react with CO_2 to form carbamates (Ooi et al., 2020). This reaction is reversible; therefore, the amine solvent can be regenerated for subsequent absorption use.

Table 2: Primary, secondary, and tertiary amine reactions with CO_2 (Ooi et al., 2020).

Amine type	Form	Reaction with CO_2
Primary amines	Direct	$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+$
Secondary amines	Direct	$CO_2 + R_1R_2NH + H_2O \leftrightarrow R_1R_2NH_2 + HCO_3^-$
Tertiary amines	by stages	$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$ $HCO_3^- \rightleftharpoons H^+ + CO_3^-$ $H^+ + R_1R_2R_3N \leftrightarrow R_1R_2R_3NH^+$

3. Effects of the composition and amines structure

To analyze the effects of concentration in amine-based solutions (MEA, DEA, MDEA, AMP, PZ) under saturation conditions at 80 °C on the corrosion rate of carbon steel 1018 (CS 1018), a carried out a research work where it was observed that the primary amine MEA presents the highest corrosion rate (4.17 mm/y), this was due to the formation of carbamates among its main reaction products, followed by the amines AMP, DEA, PZ and finally the MDEA, this being the lowest (0.89 mm/y), as shown in table 3 (Gunasekaran et al., 2017).

Table 3: Effect of amine concentration on pH and corrosion rate in CS 1018 carbon steel (Gunasekarana et al., 2017)

Amine type	Conditions	Concentration (mol CO_2/ amine)	pH	Corrosion rate (mm/y)
MEA	5.0 kmol amine solution/m^3 80 °C	0.53	8.48 ± 0.03	4.17 ± 0.02
DEA		0.40	8.41 ± 0.04	2.37 ± 0.03
MDEA		0.14	8.85 ± 0.07	0.89 ± 0.07
AMP		0.51	8.95 ± 0.13	3.11 ± 0.08
PZ		0.82	8.46 ± 0.03	1.64 ± 0.02

In a study considering an exposure time of 4 years, researchers evaluated the corrosion generated on AISI 1018 carbon steel using an MEA amine solution for CO_2 capture under pilot conditions. High corrosion rates (4.5 mm/y – 8.5 mm/y) were determined, causing a loss of almost 80 % of its initial weight (Ooi et al., 2020).
On the other hand, it has been reported that the corrosivity of carbon steel increases with the increase in the concentration of the amine, taking the MEA amine as a case study, it has been shown that concentrations greater than 30 % present high risks of corrosion in industrial plants (Ooi et al., 2020).
The relationship between the amine structure and corrosion rates was studied in a carbon steel (CS) 1018 by evaluating Tafel curves. It was determined that the corrosion rate decreases with the increasing number of substituents on the amino groups and a structural change from linear to cyclic amines, which can increase the absorption capacity. The corrosion rate generally decreases when the amine structure changes from linear to cyclic (Li et al., 2020). When this occurs, a dense $FeCO_3$ protective film is produced on the steel surface. The research results suggest that the formation of a protective film of the species depends on the carbonate/carbamate ratio.

4. Effects of temperature and pressure

Experimental evaluation and modelling of CO_2 absorption were carried out in a high-pressure column (4 MPa) using an MDEA solution, which had as one of its main objectives to measure the absorption capacity of this amine under temperatures between 30 - 70 °C. When the temperature reached 60 °C, the maximum capture efficiency (98.2 %) was achieved under a pressure of 4 MPa. However, it can be seen that at temperatures greater than 50 °C, the CO_2 absorption capacity of the amine did not increase markedly, so it was concluded that working at higher temperatures did not generate a significant benefit in the process. Still, it did generate an increase in the costs of the same CO_2 (Shahid et al., 2021).
In a research carried out, the effect of the temperature of the solution on the efficiency of CO_2 capture was determined, the study solution was a poor solution of MEA. A proportional relationship between temperature and absorption efficiency was significantly observed when the temperature increased from 25 °C to 50 °C. According to the authors, at temperatures above 50 °C, there was no significant impact on capture efficiency (Joel et al., 2014).
According to research, the absorption capacity can be improved by increasing the gas pressure. Tan et al. (2015) reported that the CO_2 absorption performance increases gradually with increasing pressure in an aqueous solution of MEA. Their results showed that removal of approximately 76 % of CO_2 is achieved when the pressure is 0.1 MPa and increases to 95 % when it rises to 1 MPa. This phenomenon was attributed to the Marangoni effect whereby the increase in partial pressure increases the concentration of CO_2 at the gas/liquid-phase interface; such a condition disrupts the interface and thus promotes the absorption rate (Tan et al., 2015).

In research work, the behaviour of an API 5L X65 carbon steel was evaluated by varying the pH, temperature, partial pressures of CO_2, and flow rate. Polarization curves were obtained at pH four and five, in which the influence of CO_2 on the cathodic and anodic curves is noted. The results show that the direct reduction of carbonic acid is not significant at partial pressures of CO_2 up to 0.5 MPa because carbonic acid acts as a reservoir for hydrogen ions. Its presence only increases the limiting current densities observed by quenching the H^+ concentration at the metal surface. It was also found that increasing the partial pressure of CO_2 up to 0.5 MPa only slightly increases corrosion rates. Thus determining that for the temperature of 30 °C in the pH four and pH 5, a higher rate of corrosion is observed than that corresponding to the temperature of 10 °C; It is also established that, for partial pressure of 5 bar, there is a higher corrosion rate compared to pressures lower than this, in the pH five system (Kahyarian et al., 2018).

5. Conclusions

This research work studied the effects of composition, the structure of amine, pressure, and temperature on CO_2 capture efficiency and corrosion of carbon steels using amine-based solvents.
According to the review, primary amines-based solvents generally present a better CO_2 capture efficiency, however, they tend to have higher corrosion rates in carbon steels. This is mainly due to the formation of carbamates when these amines react with CO_2.
Corrosion rates decrease with the increasing number of substituents on amino groups and the switching from linear to cyclic amines, which can increase absorption capacity. Corrosion rates decreased when amine structures changed from linear to cyclic. Using amine solvents as CO_2 capture processes, an equilibrium temperature value provides an adequate CO_2 efficiency vs energy cost ratio. Once this value is exceeded, there is no significant increase in CO_2 capture efficiency, but the energy costs of the process increase drastically.
The partial pressure of CO_2 increases the corrosion rate in carbon steels due to changes in the anodic reaction rates.

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