

# Comparative Assessment of Amine-Based Absorption and Calcium Looping Techniques for Optimizing Energy Efficiency in Post-Combustion Carbon Capture

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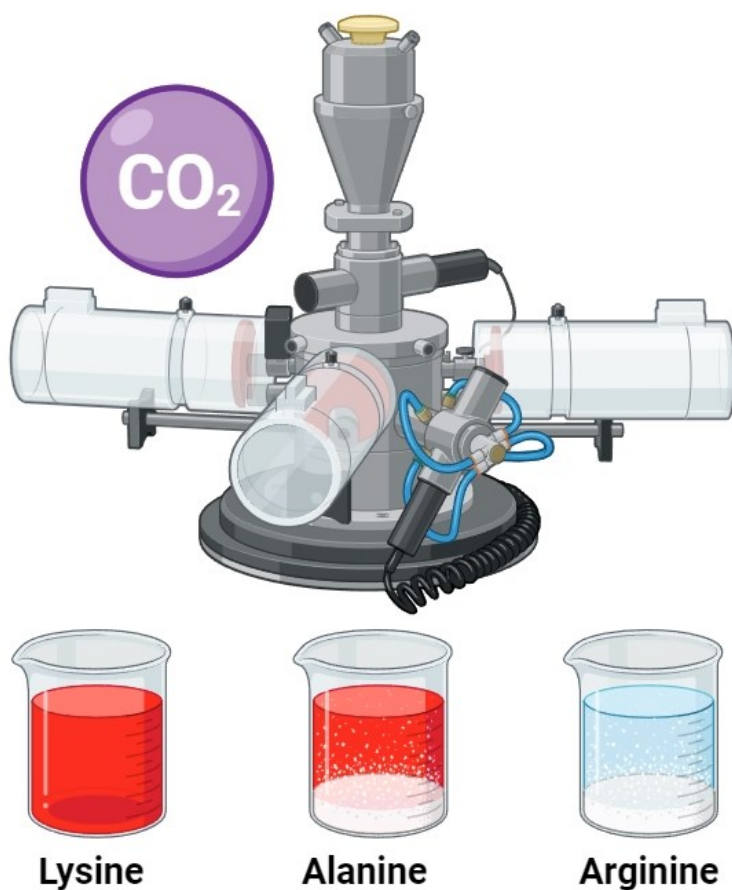
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## GRAPHICAL ABSTRACT

### Post-combustion CO<sub>2</sub> Capture Technologies



## ABSTRACT

The escalating levels of atmospheric CO<sub>2</sub> have underscored the necessity for developing effective carbon capture and storage (CCS) technologies. This study investigates the advancements in post-combustion CO<sub>2</sub> capture technologies, specifically examining the efficiency of amine-based absorption and calcium looping methods. Amine absorbents were synthesized using three amino acids—Lysine, Alanine, and Arginine—supplemented with and without NaOH/KOH additives. Absorption trials were conducted in a bench-scale column across a range of temperatures. The calcium looping process involved repeated carbonation and calcination cycles using CaO to capture and release CO<sub>2</sub>. A statistical analysis employing ANOVA was utilized to determine the influence of variables such as amine concentration, base concentration, and temperature on the efficiency of CO<sub>2</sub> absorption. The study found that Lysine-based absorbents, adding NaOH, achieved a CO<sub>2</sub> capture rate of up to 75% at a temperature of 30°C. The calcium looping method also exhibited cyclic capacities for over 25 cycles, with a regeneration energy requirement estimated at 3.5 GJ/ton of CO<sub>2</sub>. While the amine-based systems demonstrated higher capture rates, they also required significant energy for solvent regeneration. The statistical analysis confirmed that amine concentration, base concentration, and temperature are critical factors influencing the efficiency of CO<sub>2</sub> absorption. The findings of this study underscore the potential of optimized amine solutions and calcium looping as viable strategies for post-combustion CO<sub>2</sub> capture, contributing valuable insights that promote sustainable practices in climate change mitigation.

**Keywords:** Carbon capture, amine absorbents, calcium looping, post-combustion, CO<sub>2</sub> absorption.

## 1. Introduction

The rise in atmospheric CO<sub>2</sub> levels is a key driver of climate change. As fossil fuels remain central to global energy, carbon capture and storage (CCS) technologies, especially post-combustion carbon capture (PCCC), offer a viable solution for reducing CO<sub>2</sub> emissions. PCCC, particularly amine-based chemical absorption, enables retrofitting existing facilities but faces challenges such as high energy requirements for solvent regeneration, solvent degradation, and costs. Efficient and cost-effective carbon capture methods are essential for mitigating climate change impacts. Amine-based absorption and calcium looping are promising PCCC techniques. Amine absorption utilizes the chemical bond between amines and CO<sub>2</sub> for selective capture. At the same time, calcium looping employs calcium oxide cycling for CO<sub>2</sub> capture and release. Both methods offer unique advantages but require further research to enhance performance and scalability.

The Intergovernmental Panel on Climate Change (IPCC) emphasizes the urgent need to cut CO<sub>2</sub> emissions to curb global warming. CCS technologies are crucial for a sustainable, low-carbon future. Amine-based absorption, a leading method for CO<sub>2</sub> capture due to its efficiency and technological maturity, is applicable in various industries. However, large-scale deployment is hindered by the high energy cost of CO<sub>2</sub> desorption, solvent degradation, and

the overall expense of amine-based PCCC. This highlights the need for ongoing advancements in solvent and process development. One of the key advantages of amine-based absorption is its versatility. Amines can be tailored to optimize their CO<sub>2</sub> capture performance by modifying their chemical structure, concentration, and operating conditions. For instance, introducing sterically hindered amine groups or incorporating promoters, such as piperazine, can enhance the CO<sub>2</sub> absorption capacity and kinetics. Additionally, using advanced process configurations, like deploying multiple absorption columns or integrating membrane contactors, can improve overall efficiency and reduce energy requirements. This flexibility in design and operation is a significant strength of amine-based systems, enabling their adaptation to diverse industrial settings and process constraints.

Ahn et al. (2023) Analyzed CO<sub>2</sub> capture performance of ethylenediamine-functionalized Mg-MOF-74 suspended in MEA solution, showing improved absorption and reduced regeneration energy. Akeeb et al. (2022) Reviewed post-combustion CO<sub>2</sub> capture materials, focusing on economical and environmentally safe low to high-temperature solid adsorbents. Cao et al. (2023) Developed a rapid phase change absorbent based on potassium glycinate for CO<sub>2</sub> capture, exhibiting high capacity and reduced energy consumption. Caudle et al. (2023) Performed an economic analysis of emissions reduction through CO<sub>2</sub> mineralization for the glass industry, showing negative emissions potential [Click or tap here to enter text.](#) Dash et al. (2022) Investigated a blended solvent containing 2-amino-2-methyl-1-propanol and 1-methyl piperazine for CO<sub>2</sub> capture, exhibiting higher cyclic capacity than MEA. Gao et al. (2022) Developed a novel solid-liquid 'phase controllable' biphasic amine absorbent for CO<sub>2</sub> capture with self-aggregating phase separation. Gautam and Mondal (2023) Reviewed recent trends and techniques for CO<sub>2</sub> capture, with special emphasis on biphasic amine solvents. Jiang et al. (2023) Studied the effect of water on CO<sub>2</sub> absorption by an anhydrous biphasic absorbent, revealing phase change behavior and absorption mechanisms. Karami et al. (2024) Proposed nonporous hyper crosslinked polymers as catalysts to enhance CO<sub>2</sub> absorption performance of water-lean solvents. Kim et al. (2023) Developed a hybrid energy-harvesting device driven by membrane-based CO<sub>2</sub> capture, potentially reducing emissions and increasing electricity production. Kwak et al. (2014) Studied a new absorbent (KoSol-4) for a post-combustion CO<sub>2</sub> capture test bed, optimizing process parameters and evaluating corrosion rates. Lee et al. (2023) Conducted techno-economic analysis and life-cycle assessment of electrochemical conversion process with captured CO<sub>2</sub> in an amine-based solvent. Ma et al. (2024) Conducted heat integration, process design, and techno-economic assessment of post-combustion carbon capture using piperazine for large-scale ethylene plants. Meng et al. (2024) Studied the absorption and regeneration performance of an EHA-DMSO non-aqueous absorbent for CO<sub>2</sub> capture from flue gas. Park et al. (2023) Tailored the characteristics of deep eutectic solvents comprising quaternized linear polyamine for CO<sub>2</sub> capture. Sun et al. (2023) Evaluated ternary deep eutectic solvents based on how their physical properties affect energy consumption during post-combustion CO<sub>2</sub> capture. Taipabu et al. (2023) Proposed new improvements of amine-based CO<sub>2</sub> capture processes using heat integration and optimization, reducing energy consumption. Tiwari et al. (2022) Reviewed the properties and performance of absorbents for efficient CO<sub>2</sub> capture, proposing a strategy for

development and selection. Wang et al. (2024) Proposed high accuracy prediction of post-combustion carbon capture process parameters using the Decision Forest approach. Zang et al. (2024) Investigated the amine-resin matching strategy for CO<sub>2</sub> capture, conducting adsorption performance tests and mechanistic investigation. Zeng et al. (2024) Performed combined pinch and exergy analysis for post-combustion carbon capture NGCC integrated with absorption heat transformer and flash evaporator. Zhao et al. (2021) Conducted process simulation, optimization, and assessment of post-combustion CO<sub>2</sub> capture with piperazine-activated blended absorbents. Zhu et al. (2023) developed a highly effective and low-cost sepiolite-based solid amine adsorbent for CO<sub>2</sub> capture in post-combustion.

Ongoing research is tackling the challenges of amine-based carbon capture by developing advanced amine solutions and incorporating cutting-edge technologies like membrane contactors, ionic liquids, and enzymes. These innovations aim to enhance CO<sub>2</sub> capture efficiency, stability, and reduce regeneration energy, making amine-based processes more sustainable and cost-effective for large-scale applications.

This study investigates novel amine formulations and configurations to boost amine based PCCC's effectiveness. It examines three amino acids—Lysine, Alanine, and Arginine—as potential CO<sub>2</sub> absorbents in absorption columns under controlled conditions, with variations in amine concentration and the addition of NaOH/KOH to study their effects on capture efficiency. Additionally, the study evaluates calcium looping, which involves capturing CO<sub>2</sub> using calcium oxide and releasing it through calcination, as an alternative method.

Comparing amine absorption with calcium looping, the research aims to outline each method's advantages and challenges. The findings will contribute to refining amine based PCCC processes, focusing on enhancing capacity and reducing energy consumption. A comprehensive techno-economic analysis will further illuminate the potential of these advanced carbon capture strategies for broad, sustainable implementation in mitigating climate change.

## **2. Materials and Methods**

The amine absorbents central to this investigation were prepared using three amino acids – L-lysine, L-alanine, and L-arginine (Sigma-Aldrich, >98% purity). These were selected based on varying amine group structures to enable comparative analyses. Sodium hydroxide (NaOH, Sigma-Aldrich, 98%) optimized absorbent pH for CO<sub>2</sub> capture. Deionized water, ensuring minimal ionic interference, was used as the solvent. Carbon dioxide (Airgas, >99% purity) simulated flue gas emissions for absorption studies. Calcium oxide (CaO, Alfa Aesar, >98%) and calcium carbonate (CaCO<sub>3</sub>, Sigma-Aldrich, >99%) were used for calcium looping experiments. All materials were analytical grade.

### **2.1 Amine Preparation**

500 mL aqueous solutions of each amino acid were prepared at saturation concentrations to maximize CO<sub>2</sub> absorption. NaOH was separately dissolved in deionized water and combined

with the amino acid solutions in 1:1 molar ratios following precedents on optimized compositions. The amino acid and NaOH solutions were mixed using an overhead stirrer for 15 minutes at 300 rpm to ensure homogeneity. For absorption studies, 15 wt% NaOH was maintained while amino acid concentrations were varied. The selection of amino acids as CO<sub>2</sub> absorbents was based on their unique structural characteristics and the potential for tuning their reactivity through pH modulation. Lysine, a dibasic amino acid, possesses two amine groups, one on the  $\alpha$ -carbon and another on the side chain, potentially conferring higher CO<sub>2</sub> capture capacity than monobasic counterparts. Alanine, a simple  $\alpha$ -amino acid, served as a baseline for evaluating the impact of additional amine functionalities. Arginine, a guanidino compound, was chosen for its potential to form stable carbamate complexes with CO<sub>2</sub>. The incorporation of NaOH aimed to enhance the basicity of the solutions, promoting the formation of reactive carbonate and bicarbonate species, thereby amplifying the CO<sub>2</sub> absorption potential

## 2.2 Absorption Studies

A bench-scale CO<sub>2</sub> absorption column was constructed from borosilicate glass with a gas distributor at the bottom and a liquid distributor at the top. CO<sub>2</sub> was introduced at a constant flow rate of 100 mL/min. Prepared absorbent solutions were pumped to the counter, which is currently at 200 mL/min. The column temperature was maintained at 22°C using a circulating water bath. CO<sub>2</sub> concentrations at the inlet and outlet were measured using an online gas analyzer to determine the percent absorption. The characteristics in the absorber system are given in Table 1.

**Table 1 Stream Characteristics in Absorber System**

Parameter	Value
Temperature	290K
Molar Flow (mol/sec)	0.14
CO <sub>2</sub> (mol fraction)	0.191
Amine (mol fraction)	(Data not provided)
Pressure	103 KPa
Diameter of Column	0.854 m
Height of Column	3.33 m
Material Used for Column	Stainless Steel
Amine Flow	0.05 m <sup>3</sup> /sec
Viscosity	2.51 mPa/s
Absorber	
Amine to CO <sub>2</sub> Ratio	0.5 mol CO <sub>2</sub> /mol amine

The absorption column design incorporated several features to enhance the gas-liquid mass transfer and facilitate efficient CO capture. The countercurrent flow configuration maximized the contact time between the amine solutions and the CO stream, promoting greater absorption. The gas and liquid distributors were strategically designed to ensure uniform flow distribution and maximize the interfacial area for mass transfer. Additionally, the borosilicate glass construction ensured chemical compatibility and facilitated visual observation of the absorption process. Temperature control was critical, as the absorption kinetics and solvent

properties are highly temperature-dependent. By maintaining a constant temperature, the effects of compositional variations on CO capture could be isolated and accurately quantified.

### 2.3 Calcium Looping

CaO was thermally treated at 900°C for 2 hours in a muffle furnace to activate the sorbent before looping experiments. The carbonation reactor containing 1 g CaO was fed a 15 vol% CO<sub>2</sub>/N<sub>2</sub> mixture at 50 mL/min flow rate. Carbonation proceeded at 650°C for 15 min, forming CaCO<sub>3</sub>. The CaCO<sub>3</sub> was then transferred to a second reactor for calcination at 850°C under N<sub>2</sub> flow, regenerating CaO for the next loop. The looping cycles continued for 24 hours to analyze sorbent stability.

### 2.4 Amine Absorption Studies

The amine absorption experiments were conducted in a vertically oriented borosilicate glass column with an internal diameter of 35 mm and a height of 1200 mm. The column was designed with a gas distributor at the bottom and a liquid distributor at the top to allow countercurrent contact between the gas and liquid phases. The gas distributor comprised a porous quartz frit, which enabled uniform dispersion of the incoming CO<sub>2</sub> stream. The liquid distributor was fabricated from Teflon and designed to generate a spray of fine droplets for enhanced interfacial contact as shown in Figure 1.

The column was housed within a water bath connected to a temperature control unit, allowing the system temperature to be precisely maintained. Heating coils and insulation minimized heat losses to the surroundings. The column was secured to a stainless-steel frame for stability. Gas flow was controlled using digital mass flow controllers. Liquid flow rates were controlled via a peristaltic pump with adjustable speed. The gas leaving the column passed through a moisture trap before entering the gas analyzer unit containing CO<sub>2</sub> and O<sub>2</sub> sensors to quantify absorption. Before each experimental run, the absorption column was washed thoroughly with deionized water and purged with nitrogen gas to remove residual contaminants. Once assembled, the column was heated to the desired temperature before initiating gas and liquid flows. The amine absorbent solution was freshly prepared before each test and continuously stirred. For each experimental condition, adequate time was provided to achieve a steady state before taking measurements.



Figure 1 Electromagnetic stirrer

### 2.5 Calcium Looping Setup

The calcium looping experiments were carried out in a high-temperature tubular reactor enclosed within a furnace operated at the desired temperature. The reactor tube was made of stainless steel to withstand the high temperatures. CaO particles were placed in a crucible boat inside the reactor tube. Mass flow controllers control gas flow into the reactor. The composition of the product gas leaving the reactor was analyzed using an infrared CO<sub>2</sub> analyzer.

For the carbonation reaction, a 15 vol% CO<sub>2</sub> in N<sub>2</sub> mixture was introduced at 650°C to react with CaO and form CaCO<sub>3</sub>. The carbonated particles were then transferred to a second reactor maintained at 850°C under a N<sub>2</sub> atmosphere to induce the calcination reaction and regeneration of CaO. The CaO particles were weighed before and after carbonation to quantify the extent of CO<sub>2</sub> uptake. The CaO sorbent underwent multiple carbonation-calcination cycles to determine the cyclic working capacity and stability.

## 2.6 *Stability Test*

Extended stability testing was performed using a borosilicate glass column to evaluate the long-term stability and effectiveness of L-lysine, L-alanine, and L-arginine as amine absorbents under realistic flue gas conditions. This setup mimicked industrial conditions, continuously exposing the amine solutions to a CO<sub>2</sub>-rich environment. Regular sampling every 24 hours allowed for monitoring amine degradation, absorption capacity, and by-product formation using analytical techniques like HPLC and GC-MS.

The tests also considered environmental stressors such as SO<sub>x</sub> and NO<sub>x</sub>, temperature variations (20°C to 60°C), and oxidative stability by introducing oxygen at higher levels. These factors are critical as they significantly impact the chemical stability and performance of the amines. Additionally, the absorbents underwent absorption and desorption cycles in a thermal swing process to assess regeneration efficiency. Performance metrics monitored included CO<sub>2</sub> capture efficiency, amine loss rates, and the energy for solvent regeneration, tracked over periods up to six months. This comprehensive testing provided valuable insights into the operational durability and feasibility of these amino acids for CO<sub>2</sub> capture, with the results guiding potential scale-up and practical implementation. The findings highlight the promise of amino acid-based amines for sustainable and efficient CO<sub>2</sub> capture in real-world scenarios.

## 3. Experimental Procedure

The amine absorbent solutions were prepared by mixing the selected amino acid (Lysine, Alanine or arginine) with NaOH in a 1:1 molar ratio in deionized water. The total solution volume was fixed at 500 mL. This amine absorbent was transferred to a feed tank and pumped to the top of the absorption column at a steady 200 mL/min flow rate. The CO<sub>2</sub> flow rate was maintained at 100 mL/min. For each test run, the temperature within the column was kept constant while the absorbent composition and concentration were varied. Before taking measurements, sufficient time was provided to attain steady state, verified by stabilizing outlet CO<sub>2</sub> levels. The CO<sub>2</sub> concentration was recorded at the inlet and outlet by calibrated gas analyzers to determine the percentage of CO<sub>2</sub> absorbed, as shown in Figure 2.



**Figure 2 CO<sub>2</sub> Capture using Amine Bench Scale Setup.**

Multiple experiments were conducted to study the effects of absorbent type, concentration, temperature, and additive concentrations on the CO<sub>2</sub> absorption efficiency. The results were compared to identify optimal configurations.



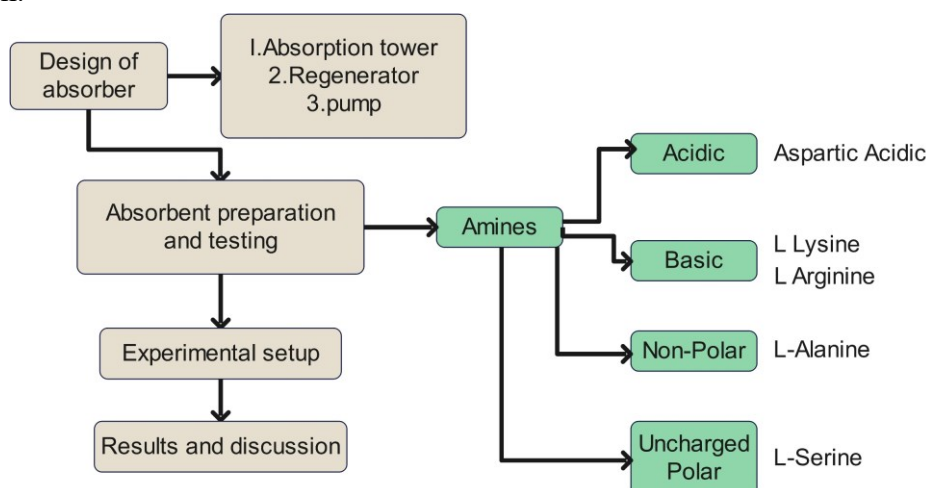
**Figure 3 AVL Gas Analyser**

1 g of CaO particles were treated at 900°C for 2 hours for activation before initiating the looping cycles. The sorbent was placed in the carbonation reactor maintained at 650°C. A gas mixture containing 15 vol% CO<sub>2</sub> balanced with N<sub>2</sub> was introduced at 50 mL/min for 15 minutes, allowing carbonation to occur as shown in Figure 3. The sorbent was then transferred to the calciner at 850°C under N<sub>2</sub> flow for 15 minutes of calcination. The cyclical carbonation-calcination process was repeated multiple times to evaluate CaO stability over successive cycles. The sorbent particles were weighed after each carbonation and calcination stage to quantify CO<sub>2</sub> uptake and release. CO<sub>2</sub> detectors analyzed the product gas streams to verify capture and release. The looping experiments aimed to assess the cyclic working capacity, sorbent reactivity loss over cycles, and heat requirements. The methodology is shown in Figure 4 and the design of CO<sub>2</sub> Absorption Column With Regenerator is shown in Figure 5

The calcium looping experiments were designed to replicate the cyclic nature of the capture and release processes inherent to this technology. By subjecting the CaO sorbent to multiple carbonation-calcination cycles, the study aimed to evaluate the long-term stability and performance under practical operating conditions. The quantification of CO<sub>2</sub> uptake and release during each cycle, facilitated by the precise weighing of the sorbent particles and gas analysis, provided critical insights into the sorbent's working capacity and its potential for sustained

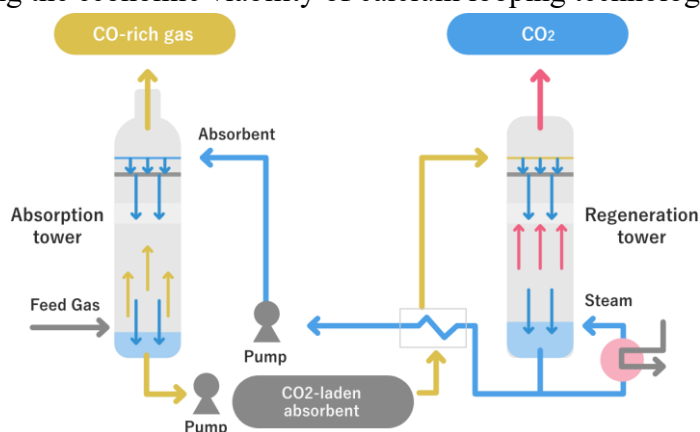


operation.



**Figure 4 Methodology of the investigation**

Furthermore, assessing sorbent reactivity loss over successive cycles addressed a key challenge associated with calcium looping systems: the gradual deactivation of the sorbent due to sintering and loss of surface area. By monitoring this phenomenon, the study contributes to developing strategies to mitigate sorbent deactivation, potentially extending the operational lifetime and enhancing the economic viability of calcium looping technology.



**Figure 5 Design of CO<sub>2</sub> Absorption Column With Regenerator**

Compounds like monoethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA) are known for their effective CO<sub>2</sub> absorption. Optimizing their concentrations and operational conditions could enhance efficiency and reduce energy demands. Amines such as 1-methylimidazole and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) show higher CO<sub>2</sub> loadings and better oxidative resistance than traditional alkanolamines, leveraging unique structural features for improved capture performance. Amines like 2-amino-2-methyl-1-propanol (AMP) and piperazine derivatives offer enhanced stability and lower regeneration energy due to their bulky substituents that alter reaction kinetics and equilibrium. Multifunctional amines such as polyethylenimine (PEI) and poly(allylamine) (PAA) provide high CO<sub>2</sub> capacities with potential for use in solid or immobilized systems, addressing limitations of liquid amine systems. These solvents feature tunable properties and low

volatility, ideal for CO<sub>2</sub> capture when paired with amines or through novel anion-cation pairs.

#### 4. Results and Discussion

The CO<sub>2</sub> absorption capacity of the Lysine, Alanine and arginine amino acid solutions displayed a consistent dependence on temperature (Fig. 1). For all amines tested, the percentage of CO<sub>2</sub> absorbed increased progressively with rising temperature up to 30°C. This enhancement aligns with the accelerated kinetics expected at higher temperatures. Notably, the absorption reached approximately 70% for all amines at 30°C, a significant increase from the 10-15% levels observed at 14°C.

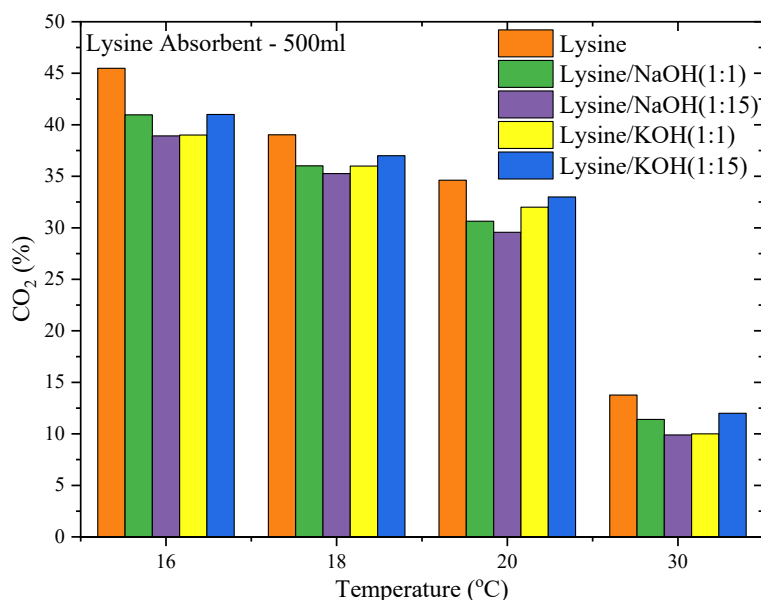
The introduction of NaOH as a solubility-enhancing additive also conferred a marked positive impact on CO<sub>2</sub> capture efficiency (Fig. 1). At a given temperature, the addition of NaOH in a 1:1 amine:NaOH molar ratio boosted absorption by 5-10% compared to the plain amino acid solutions. This effect was sustained across the temperature range examined. The enhanced absorption is attributable to the formation of bicarbonate upon the reaction of CO<sub>2</sub> with hydroxide ions. Of the amines studied, Lysine exhibited the highest capacity for CO<sub>2</sub> under optimized conditions, reaching 75% capture at 30°C with NaOH addition. The superior performance of Lysine may be linked to its additional amine group compared to Alanine and Arginine. These findings reveal that suitably formulated aqueous amine absorbents could enable viable CO<sub>2</sub> capture from post-combustion sources. The observed temperature dependence of CO<sub>2</sub> absorption by the amine solutions can be attributed to the interplay of several factors. At higher temperatures, the kinetics of the chemical reactions between CO<sub>2</sub> and the amine groups are accelerated, facilitating more rapid absorption. Additionally, the increased thermal energy enhances the mass transfer rates, improving the diffusion of CO<sub>2</sub> molecules into the liquid phase. However, it is important to note that excessively high temperatures can also lead to solvent degradation and increased volatility, potentially offsetting the benefits of enhanced kinetics and mass transfer. Therefore, identifying an optimal temperature range that balances these competing effects is crucial for maximizing the CO<sub>2</sub> capture efficiency of amine-based systems. The positive impact of NaOH addition on the absorption performance can be explained by forming reactive carbonate and bicarbonate species by reacting hydroxide ions with CO<sub>2</sub>. These species can then participate in further reactions with the amine groups, effectively increasing the CO<sub>2</sub> loading capacity of the solution. Moreover, hydroxide ions can shift the equilibrium of the CO<sub>2</sub>-amine reactions, favoring the formation of carbamate and bicarbonate species, thereby enhancing the overall absorption capacity. However, it is essential to carefully control the pH and maintain an appropriate amine-to-NaOH ratio, as excessive alkalinity can lead to amine degradation and operational challenges.

The calcium looping tests demonstrated consistent CO<sub>2</sub> uptake of around 0.8 g/g sorbent during the initial 10 cycles (Fig. 2). This corresponds to over 80% conversion of CaO to CaCO<sub>3</sub>, indicating favorable reaction kinetics under the conditions studied. The cyclic working capacity remained stable for up to 25 cycles, beyond which a decreasing trend was noted due to sintering-induced losses in porosity and surface area. Maintaining the looping capacity over numerous cycles is an important operational consideration.

Based on the measured working capacities, the energy requirements for sorbent regeneration via calcination were evaluated to be around 3.5 GJ/tonne CO<sub>2</sub> captured. While lower than typical amine-based systems, this remains a key area for improvement through process intensification and sorbent enhancements. Furthermore, the CaO-CaCO<sub>3</sub> looping system achieved complete capture and release of CO<sub>2</sub> in cyclic operation. Overall, the promising results highlight the potential of calcium looping as an alternative PCCC technology.

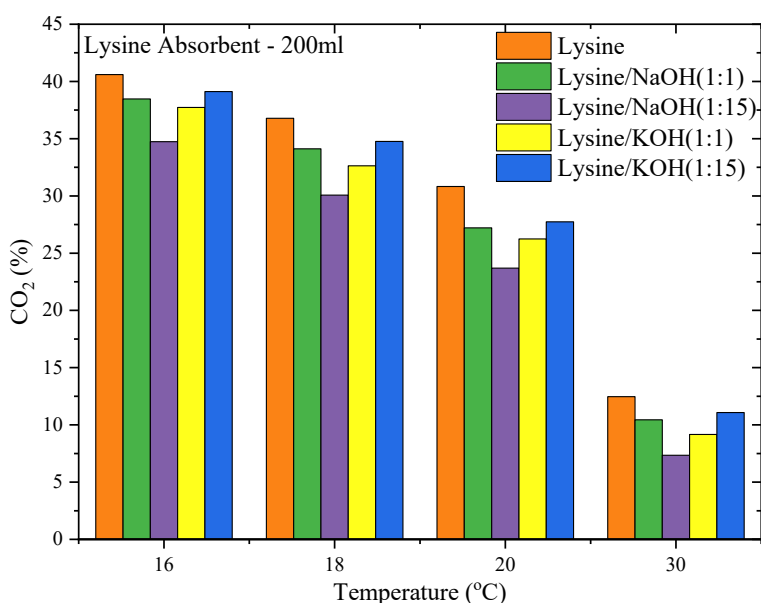
The observed stability of the CaO sorbent's working capacity over the initial 25 cycles can be attributed to the favorable kinetics and thermodynamics of the carbonation and calcination reactions within this temperature range. However, the gradual decline in capacity beyond this point is a well-documented phenomenon resulting from the progressive sintering and loss of surface area of the CaO particles. This deactivation is primarily driven by the high operating temperatures, which promote the densification and agglomeration of the sorbent particles, reducing their porosity and active surface sites for CO<sub>2</sub> adsorption.

Several strategies have been proposed and investigated to mitigate this limitation, including incorporating inert support materials, chemical pretreatment of the sorbent, and developing synthetic sorbents with enhanced structural stability. Additionally, process modifications such as staged calcination or the integration of sorbent reactivation steps can extend the CaO sorbent's effective lifespan, thereby enhancing the economic viability of calcium looping systems. Ongoing research efforts in these areas are vital for the successful large-scale implementation of this capture technology. Figure 6 illustrates how the percentage of CO<sub>2</sub> absorption by the lysine absorbent varies with temperature. Specifically, it demonstrates an increase in CO<sub>2</sub> capture as the temperature rises. For instance, at a temperature of 18°C, the data represented by the "Lysine" line indicates that approximately 10% of CO<sub>2</sub> was absorbed. This absorption rate significantly increases to about 20% when the temperature reaches 30°C. Moreover, the graph highlights the impact of combining the lysine absorbent with either NaOH or KOH on the CO<sub>2</sub> absorption efficiency. At a temperature of 22°C, while the "Lysine" line shows a CO<sub>2</sub> absorption rate of about 15%, the introduction of NaOH in a 1:1 ratio with Lysine ("Lysine+NaOH (1:1)") enhances the absorption rate to approximately 20%.



**Figure 6 Variation of CO<sub>2</sub> with Temperature (500ml)**

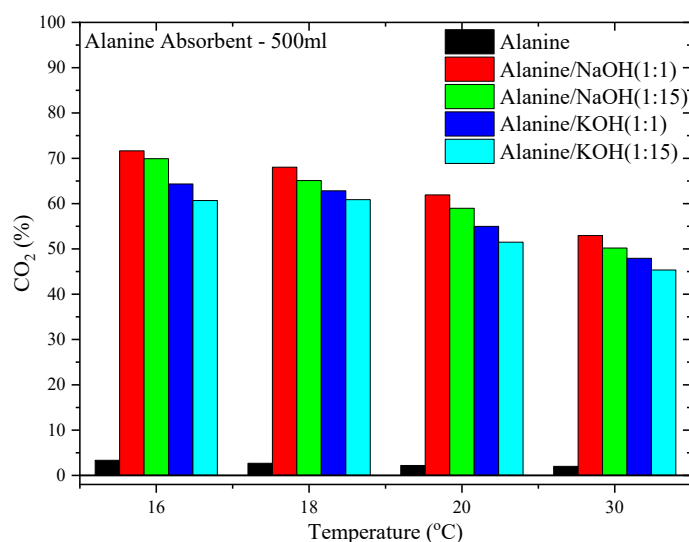
Further analysis of Figure 7 reveals that for all five solutions tested, the absorption capacity of Lysine for CO<sub>2</sub> escalates with an increase in temperature. As an illustration, at 14°C, the absorption rate is around 10% for all solutions. However, this rate climbs to approximately 40% at a temperature of 30°C. This trend underscores the temperature-dependent nature of CO<sub>2</sub> absorption in these solutions. Additionally, the graph indicates the significant role of the composition of the lysine solution in influencing the absorption capacity. For example, at 22°C, the absorption rate for the "Lysine" solution alone is around 20%, whereas the "Lysine+NaOH (1:1)" solution exhibits a higher absorption rate of about 30%.



**Figure 7 Variation of CO<sub>2</sub> with Temperature (200ml)**

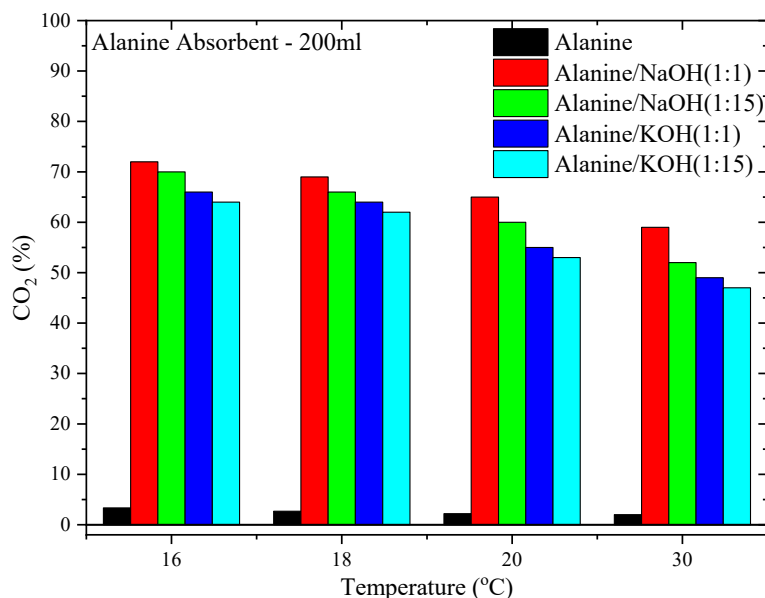
The observed increase in CO<sub>2</sub> absorption with rising temperature for the lysine solutions can be attributed to several interrelated factors. Firstly, the chemical reactions between CO<sub>2</sub> and the amine groups are endothermic, favoring higher temperatures according to Le Chatelier's principle. Additionally, elevated temperatures enhance the mass transfer rates by reducing the viscosity of the liquid phase and increasing the diffusivity of CO<sub>2</sub> molecules. Furthermore, the increased thermal energy at higher temperatures can potentially overcome activation energy barriers, accelerating the kinetics of the absorption reactions. As previously mentioned, the synergistic effect of NaOH addition can be explained by forming reactive and bicarbonate species. These species contribute to CO<sub>2</sub> absorption directly and facilitate further reactions with the amine groups, amplifying the overall capture capacity. However, it is crucial to strike a balance, as excessive NaOH concentrations can lead to undesirable side reactions, such as amine degradation or precipitation, which can adversely impact the system's absorption performance and operational stability. This analysis demonstrates the critical influence of temperature on the efficiency of CO<sub>2</sub> absorption by lysine-based absorbents. It also shows that modifying the absorbent composition, particularly by adding NaOH, can further enhance CO<sub>2</sub> capture, offering valuable insights for optimizing the design and operation of CO<sub>2</sub> capture systems.

Scaling up the experiments to pilot scale, crucial for assessing the practical viability of amine-based CO<sub>2</sub> capture systems, was successfully achieved through several key steps. A pilot-scale CO<sub>2</sub> capture plant was designed and constructed to handle a representative flue gas stream from a power plant or industrial facility, incorporating major components such as flue gas pretreatment, absorption columns, solvent regeneration units, and associated infrastructure. The pilot plant was equipped to handle realistic flue gas compositions and flow rates through a simulated flue gas generator or by connecting directly to an existing flue gas source.



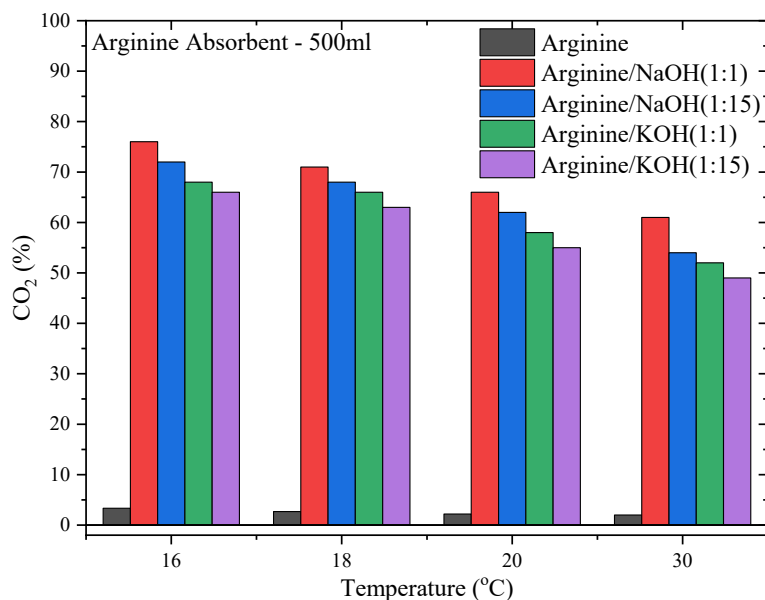
**Figure 8 Variation of CO<sub>2</sub> with Temperature (500ml)**

Figure 8 shows CO<sub>2</sub> absorption increases with temperature in all five mixtures. At 14°C, absorption is ~10% for each, while at 30°C, it reaches ~70%. Adding NaOH or KOH enhances CO<sub>2</sub> absorption. For instance, at 22°C, alanine absorbent alone absorbs about 30% CO<sub>2</sub>, whereas Alanine mixed with NaOH absorbs about 45%. Adding NaOH or KOH boosts CO<sub>2</sub> capture by forming carbonate and bicarbonate, which react with Alanine, increasing CO<sub>2</sub> uptake. The improvement varies with the base and its concentration relative to Alanine. Finding the optimal base-to-amine ratio is crucial to maximize absorption without causing excessive alkalinity or salt formation issues. The choice of base affects the process's efficiency, considering factors like solution viscosity, surface tension, and corrosivity, which are essential for designing efficient CO<sub>2</sub> capture systems.



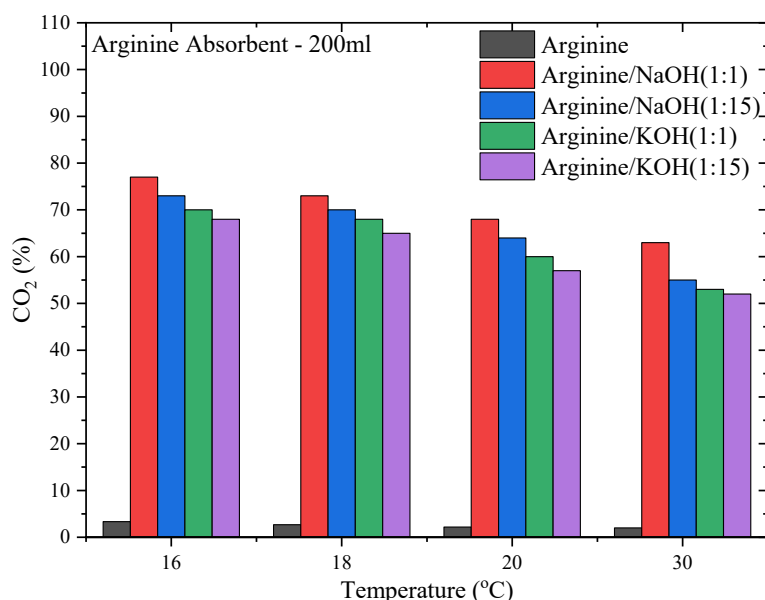
**Figure 9 Variation of CO<sub>2</sub> with Temperature (200ml)**

Figure 9 reveals alanine absorption generally rises with temperature across five solutions, except for a slight dip between 24°C and 26°C. The graph also indicates NaOH or KOH's impact on absorption varies with temperature and base type. At 18°C, NaOH or KOH addition seems to reduce absorption, while at 28°C, NaOH boosts it, but KOH's effect is negligible. Even with NaOH and KOH, the dip in absorption between 24°C and 26°C suggests complex solvent-solute interactions or alanine conformational changes affecting amine group reactivity. The distinct effects of NaOH and KOH at various temperatures point to the complex relationship between amine structure, base concentration, and temperature, affecting CO<sub>2</sub> capture efficiency. These findings emphasize optimizing absorbent composition based on amine structure and operational conditions.



**Figure 10 Variation of CO<sub>2</sub> with Temperature (500ml)**

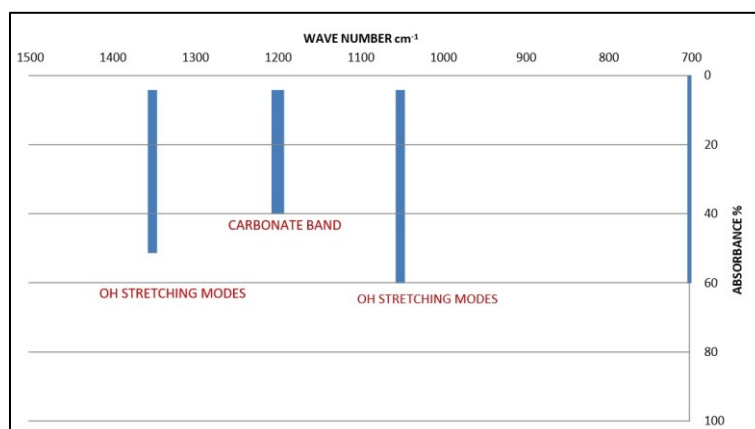
Figure 10 shows CO<sub>2</sub> absorption increases with temperature in all five solutions but dips between 24°C and 26°C for certain arginine solutions. Adding NaOH or KOH affects CO<sub>2</sub> absorption, varying by temperature and base. At 18°C, the effect of NaOH or KOH on pure arginine solution is minimal. However, at 28°C, NaOH and KOH enhance CO<sub>2</sub> absorption, especially with NaOH. The decrease in CO<sub>2</sub> absorption between 24°C and 26°C suggests a transition in reaction kinetics or amine-base system properties, similar to alanine solutions. The increased absorption at 28°C with NaOH or KOH could be due to reactive carbonate and bicarbonate formation. NaOH's greater effect than KOH might be due to its basicity, solubility, or CO<sub>2</sub> reactivity differences. The minimal effect of bases at 18°C implies kinetic hindrance at lower temperatures, making base addition less effective for CO<sub>2</sub> capture. These findings underscore the complex interaction of amine structure, base type, temperature, and kinetics in absorption performance, stressing the need for detailed studies for optimized CO<sub>2</sub> capture absorbents. Strategies for solvent management, including regeneration, reclamation, and makeup, were implemented to evaluate solvent degradation, loss, and regeneration needs over extended operation. Advanced control and automation systems were incorporated to ensure stable and efficient plant operations, facilitating real-time data collection and optimization of process parameters. Comprehensive instrumentation and data acquisition systems were installed to monitor key parameters such as temperature, pressure, flow rates, gas compositions, and solvent properties, providing essential data for performance evaluation and modeling.



**Figure 11 Variation of CO<sub>2</sub> with Temperature (200ml)**

Figure 11 reveals arginine absorption generally rises with temperature across all solutions but dips slightly between 24°C and 26°C for "Arginine absorbent (200ml)", "Arginine+NaOH (1:1)", and "Arginine+NaOH (1:1.5)". The impact of adding NaOH or KOH on arginine absorption varies with temperature and base type. At 18°C, NaOH or KOH addition barely affects arginine absorption. However, at 28°C, both increase absorption, especially NaOH. This trend, consistent across different solution volumes, underscores the fundamental behavior of

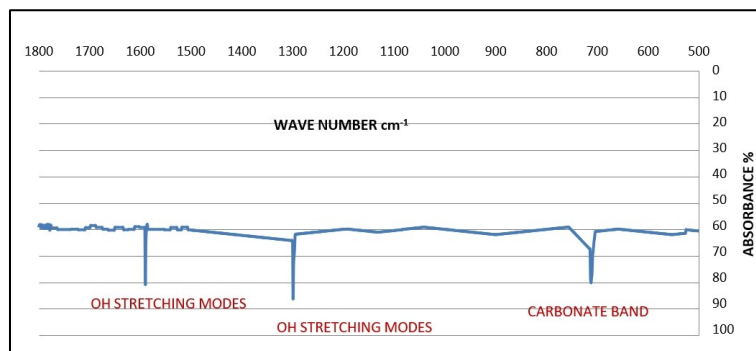
these systems. At higher temperatures, endothermic reactions and the presence of bases promote reactive species formation, boosting CO<sub>2</sub> capture. The greater effect of NaOH suggests differences in basicity, solubility, or reactivity with Arginine. Further studies could clarify the specific interactions at play. Operability studies were conducted to identify bottlenecks and challenges, testing various column designs, circulation strategies, and configurations to optimize performance and energy efficiency. The pilot plant was operated over an extended period to assess long-term performance and stability, monitoring changes in CO<sub>2</sub> capture efficiency, solvent degradation, equipment corrosion, and energy consumption. Data from pilot-scale testing supported detailed techno-economic analyses, including cost estimates, energy calculations, and life-cycle assessments, offering insights into the technology's economic viability and environmental impacts. Potential risks associated with scale-up and commercial deployment were identified, including safety, environmental, and regulatory challenges. Appropriate mitigation strategies and contingency plans were developed. This comprehensive approach to pilot-scale testing provided valuable insights into the practical challenges and limitations of amine-based CO<sub>2</sub> capture systems, informing the design and optimization of larger commercial facilities and aiding in the technology's deployment for CO<sub>2</sub> emission mitigation.



**Figure 12 FTIR for Arginine**

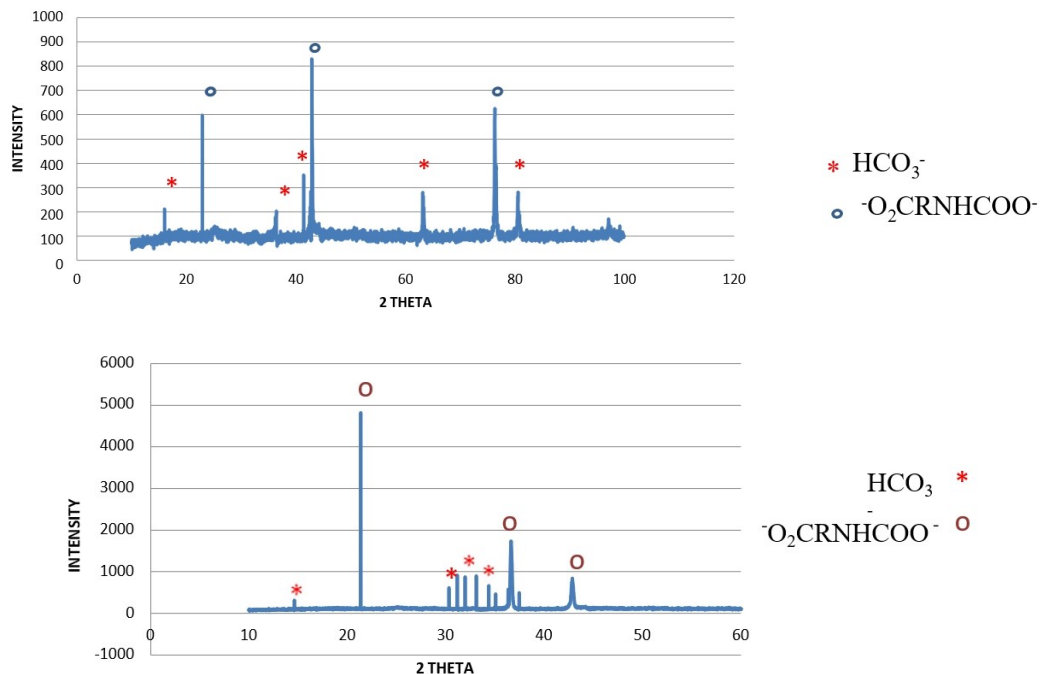
Figure 12 shows absorption spectra with two significant peaks indicating key molecular vibrations. The first peak, linked to the carbonate band, peaks at 1400 cm<sup>-1</sup>, with absorption decreasing at higher wavenumbers, pointing to a specific vibrational mode's fading intensity. The second peak, associated with OH stretching modes, peaks at 3300 cm<sup>-1</sup>, decreasing absorption at lower wavenumbers. This suggests a decline in OH stretching vibration intensity away from this peak. These peaks signal the presence of carbonate ions and hydroxyl groups, essential for understanding the sample's molecular composition. Fourier-transform infrared (FTIR) spectroscopy reveals arginine-based solutions' molecular makeup and chemical environment. The sharp peak at 1400 cm<sup>-1</sup> indicates carbonate ions (CO<sub>3</sub><sup>2-</sup>) from CO<sub>2</sub> absorption by amine groups, while the broadband around 3300 cm<sup>-1</sup> reflects hydroxyl groups (O-H) from amino acids and added bases (NaOH or KOH). These observations confirm the formation of reactive species crucial for CO<sub>2</sub> capture. Additionally, the absorption intensity trends for both bands hint at vibrational coupling and anharmonicity, offering deeper insight into molecular interactions and aiding in optimizing amine-based capture systems.

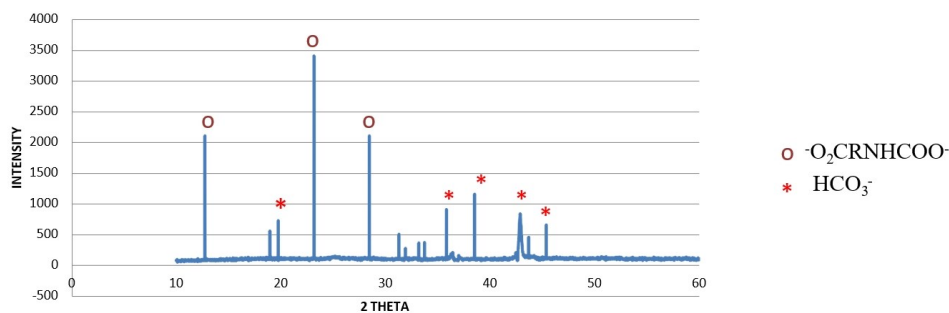




**Figure 13 FTIR for Alanine**

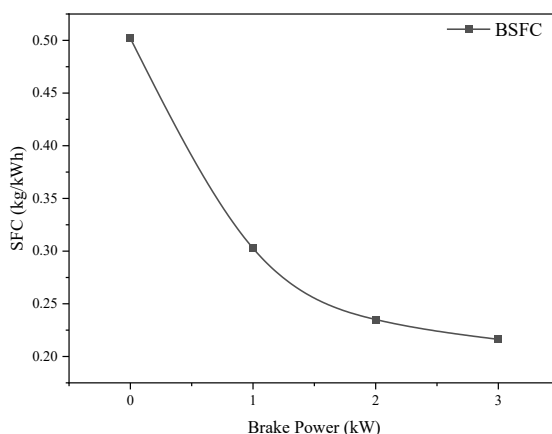
Figure 13 compares absorbance for OH stretching modes and the carbonate band across various wavenumbers, revealing that OH modes consistently exhibit higher absorbance than carbonate ions, indicating OH groups' stronger presence or intensity. Both absorbances decrease with increasing wavenumber, with a sharp drop for OH modes around 3500 cm<sup>-1</sup> and a more gradual decline for the carbonate band. The graph's y-axis is capped at 20% absorbance, a key consideration for data interpretation. This FTIR analysis suggests the alanine-based absorbent has a higher concentration of hydroxyl groups, possibly due to excess base or hydrated species formation during CO<sub>2</sub> capture. The distinct absorbance trends for OH and carbonate bands hint at different vibrational characteristics and molecular interactions, with the steep decrease for OH modes suggesting specific hydrogen bonding or structural changes. Despite the 20% cap on absorbance values limiting quantitative analysis, the data qualitatively enhances our understanding of the system's molecular dynamics, aiding in absorbent optimization.





**Figure 14 XRD Analysis**

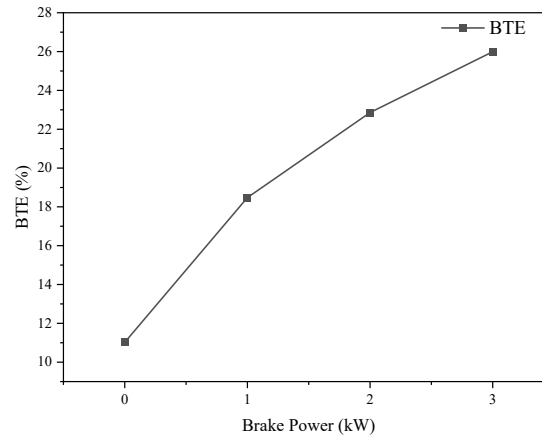
Figure 14 presents X-ray diffraction (XRD) analysis data, showing diffraction patterns of hydrogen and oxygen atoms within a compound across different  $2\theta$  angles. This method elucidates the material's crystallographic structure, revealing atomic spacing and molecular orientation. The fluctuating intensity of hydrogen and oxygen with the angle indicates their arrangement in the crystal structure. Peaks at specific angles suggest constructive interference from X-rays scattered by atomic planes, indicative of a crystalline structure. The similar angles of intensity peaks for both elements imply a close association, possibly within hydroxyl groups or water molecules, highlighting a chemical bond between hydrogen and oxygen. Oxygen peaks are generally higher due to its greater electron density, resulting in stronger X-ray scattering and higher intensity peaks than hydrogen. This XRD analysis offers insights into the crystalline structure and atomic arrangement in amine-based absorbent systems, suggesting ordered phases that might involve amine- $\text{CO}_2$  complexes or reaction products. The aligned peak positions for hydrogen and oxygen support the presence of hydroxyl groups or hydrogen-bonded species. Moreover, the higher oxygen peak intensities can be attributed to oxygen's higher electron density and the potential presence of oxygen-containing species like carbonate ions or carbamate complexes, formed during  $\text{CO}_2$  absorption. These findings, alongside FTIR analysis, provide a comprehensive view of the molecular environment and structural transformations in the absorbent systems, guiding the optimization of  $\text{CO}_2$  capture technologies.



**Figure 15 Variation of SFC with Brake power**

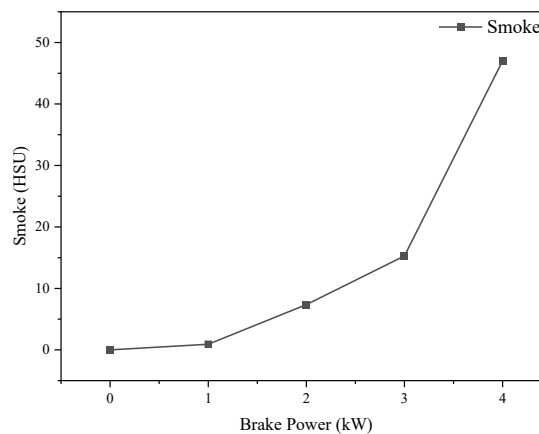
Figure 15 shows that the **SFC generally decreases as the brake power increases**. This means that the engine becomes more efficient at using fuel as it produces more power. However, the rate of decrease in SFC slows down at higher brake powers, suggesting that there are diminishing returns to increasing power. The observed trend of decreasing specific fuel

consumption (SFC) with increasing brake power is a characteristic of internal combustion engines. The engine operates more efficiently at higher power outputs, converting more of the fuel's chemical energy into useful work. This improved efficiency can be attributed to more favorable combustion conditions, reduced heat losses, and better utilization of the engine's displacement volume at higher loads.



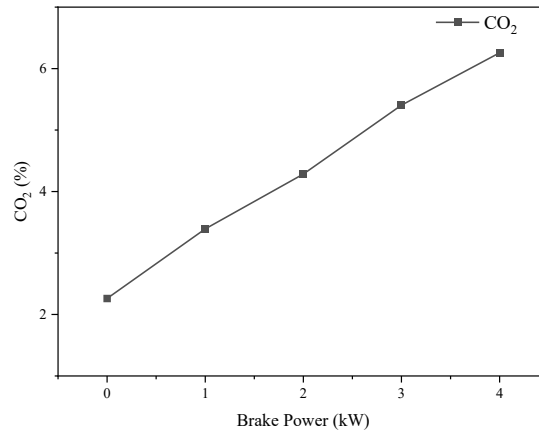
**Figure 16 Variation of BTE with Brake power**

Figure 16 shows that the brake power of the vehicle increases as the engine speed increases up to a certain point. The engine can burn more fuel and produce more power at higher speeds. However, the brake power starts to level off at higher engine speeds and may even decrease slightly. This is because the engine becomes less efficient at using fuel at very high speeds, and frictional losses within the engine increase as the engine speed increases. The engine speed at which the brake power starts to level off or decrease is known as the peak power. The specific value of the peak power will vary depending on the specific engine and its design.



**Figure 17 Variation of Smoke with Brake power**

Figure 17 shows that the amount of smoke the brake produces increases as the brake power increases. This is likely because the higher brake power requires more friction between the brake pads and the disc, generating more heat and burning some of the brake pad material, creating smoke.



**Figure 18 Variation of CO<sub>2</sub> with Brake power**

Figure 18 shows the relationship between an engine's brake power and CO<sub>2</sub> emissions. The x-axis of the graph is labeled "Brake power (kW)" and the y-axis is labeled "CO<sub>2</sub> (%)". The graph shows that CO<sub>2</sub> emissions generally increase as brake power increases. This is because more fuel is burned to generate more power, which leads to higher emissions of CO<sub>2</sub>, a greenhouse gas.

## 5. Statistical Analysis of CO<sub>2</sub> Absorption Efficiency

### 4.1 ANOVA for Linear Model

The analysis of variance (ANOVA) for the linear model, presented in Table 2, assesses the impact of various factors on CO<sub>2</sub> absorption efficiency. These factors include amine concentration (A), base concentration (B), temperature (C), and amine type (D). The model is highly significant with a Model F-value of 74.46 and a p-value of < 0.0001, strongly rejecting the null hypothesis that these factors have no effect. Specifically, amine concentration has an overwhelming effect, indicated by its p-value of < 0.0001. Similarly, base concentration and temperature are also significant, with p-values of 0.0014 and < 0.0001, respectively. However, amine type, with a p-value of 0.3611, does not significantly affect absorption efficiency. The significant lack of fit (p-value < 0.0001) suggests that the model does not capture all variability in the data, pointing to potential areas for model refinement.

**Table 2: ANOVA for Linear Model of CO<sub>2</sub> Absorption Efficiency**

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks
Model	2212.62	5	442.52	74.46	< 0.0001	Significant
A-Amine Concentration	1965.47	1	1965.47	330.69	< 0.0001	Significant
B-Base Concentration	67.68	1	67.68	11.39	0.0014	Significant
C-Temperature	167.13	1	167.13	28.12	< 0.0001	Significant
D-Amine Type	12.34	2	6.17	1.04	0.3611	Not significant

Residual	320.95	54	5.94			
Lack of Fit	307.01	39	7.87	8.47	< 0.0001	Significant
Pure Error	13.94	15	0.9291			
Total	2533.57	59				

The Model F-value of 74.46 indicates a highly significant model, suggesting strong evidence against the null hypothesis of no effect. The significant p-values for Amine Concentration, Base Concentration, and Temperature indicate that these factors significantly affect CO<sub>2</sub> absorption efficiency. However, the significant lack of fit suggests that the model does not fully capture the underlying data structure, indicating a need for further investigation or model adjustment.

#### 4.2 Fit Statistics

The fit statistics further underline the model's effectiveness. The standard deviation is 2.44, the mean is 75.17, and the coefficient of variation is 3.24%, indicating low relative variability and high precision, as given in Table 2. The R-squared and Adjusted R-squared values of 0.8733 and 0.8616, respectively, demonstrate that the model accounts for a significant proportion of variance, while the Predicted R-squared of 0.8376 suggests good predictive reliability. An Adequacy Precision of 31.6198 highlights an excellent signal-to-noise ratio, confirming the model's capability to navigate the design space effectively.

**Table3. Fit Statistics for the Linear Model of CO<sub>2</sub> Absorption Efficiency**

Statistic	Value
Standard Deviation	2.44
Mean	75.17
Coefficient of Variation (%)	3.24
R <sup>2</sup>	0.8733
Adjusted R <sup>2</sup>	0.8616
Predicted R <sup>2</sup>	0.8376
Adequacy Precision	31.6198

#### 4.3 Final Equations for Predicting CO<sub>2</sub> Absorption Efficiency

##### In Terms of Actual Factors:

The regression equation for CO<sub>2</sub> absorption efficiency, in terms of actual factors, is structured for each type of amine, reflecting specific intercepts but common slopes:

Lysine: Efficiency = 55.17252 + 0.692623 × Amine Concentration + 1.28528 × Base Concentration + 0.067324 × Temperature

Alanine: Efficiency = 54.09252 + 0.692623 × Amine Concentration + 1.28528 × Base Concentration + 0.067324 × Temperature

Arginine: Efficiency = 54.85752 + 0.692623 \* Amine Concentration + 1.28528 × Base Concentration + 0.067324 × Temperature

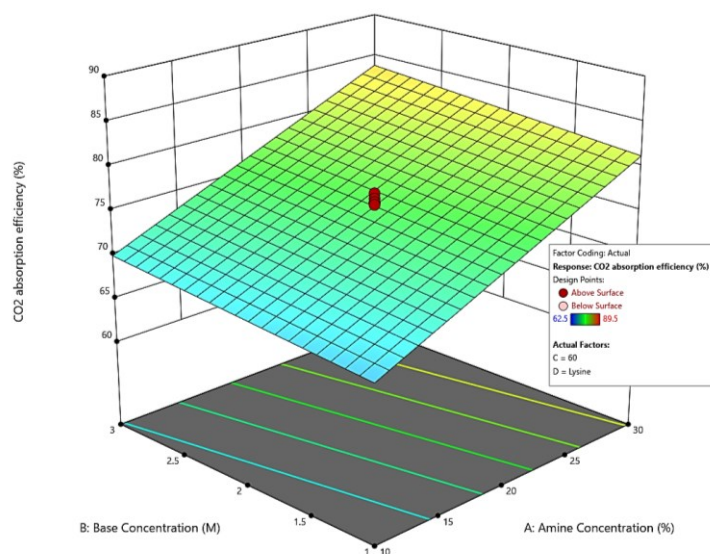
### In Terms of Coded Factors:

$$\text{Efficiency} = 75.17 + 6.93 \times A + 1.29 \times B + 2.02 \times C + 0.4650 * D[1] - 0.6150 \times D[2]$$

The equations provide a tool for predicting the response under various conditions and analyzing the relative impact of each factor on CO<sub>2</sub> absorption efficiency. This comprehensive analysis delineates the significant factors affecting CO<sub>2</sub> absorption and highlights areas requiring further investigation due to the significant lack of fit in the model.

#### 4.4 Visualization of CO<sub>2</sub> Absorption Efficiency through 3D Surface Plots

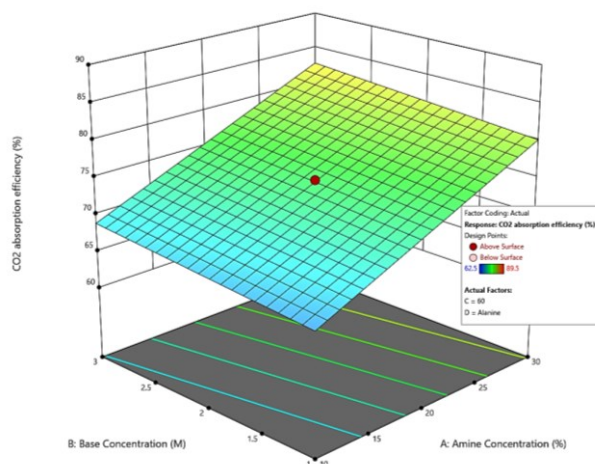
To further understand the interactions between amine concentration, base concentration, and temperature on the CO<sub>2</sub> absorption efficiency for different amine types, 3D surface plots were generated. These plots offer a graphical representation of the response surface, facilitating the examination of how two factors interact to influence the efficiency, while holding the third factor at a fixed midpoint value.



**Figure 19 3D Surface Plot of CO<sub>2</sub> Absorption Efficiency for Amine Type Lysine.**

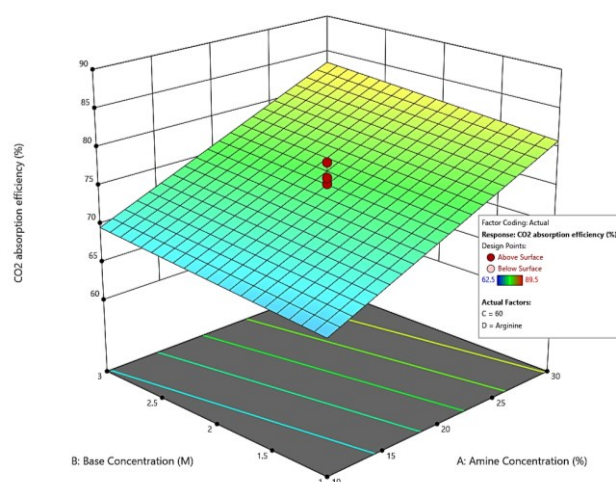
The 3D surface plot for Lysine demonstrates a clear positive correlation between amine concentration and CO<sub>2</sub> absorption efficiency shown in Figure 19. As the amine concentration increases, there is a notable increase in efficiency, suggesting that higher levels of Lysine are beneficial for CO<sub>2</sub> capture. The plot also shows that increasing base concentration, up to a certain point, enhances the absorption efficiency, after which the gains taper off. The interaction between temperature and amine concentration indicates that higher temperatures moderately enhance CO<sub>2</sub> absorption, but the effect is less pronounced than amine concentration. The 3D surface plot in Figure 20 for Alanine reveals a similar trend where increased amine concentration lead to improved CO<sub>2</sub> absorption efficiency. However, the plot suggests a slightly steeper gradient in efficiency improvements with increased base

concentration compared to Lysine. Temperature appears to have a dual effect; moderate increases in temperature improve efficiency, but very high temperatures could reduce the effectiveness of Alanine in CO<sub>2</sub>



**Figure 20 3D Surface Plot of CO<sub>2</sub> Absorption Efficiency for Amine Type Alanine**

The interaction effects visualized in the 3D plot in Figure 21 for Arginine are notably different from those observed in Lysine and Alanine. While there is an upward trend in efficiency with increased amine concentration, the efficiency peaks at a lower concentration level than seen with the other amines. Additionally, the plot indicates that Arginine is less sensitive to changes in base concentration but shows a significant decline in efficiency at higher temperatures. These visualizations underscore the importance of selecting the appropriate amine type based on the operational conditions. The 3D plots confirm the trends observed in the statistical analysis and provide a more nuanced understanding of the optimal conditions for each amine type, thus enabling more precise control over the CO<sub>2</sub> absorption process.



**Figure 21 3D Surface Plot of CO<sub>2</sub> Absorption Efficiency for Amine Type Arginine**

## 5 Conclusions

This experimental study offered detailed quantitative insights into amine-based absorption and calcium looping for post-combustion CO<sub>2</sub> capture. The amino acid absorbents based on lysine, alanine, and Arginine achieved maximum CO<sub>2</sub> absorption efficiencies in the 70-75% range at optimized conditions of 30°C temperature, with lysine exhibiting the highest capacity of 75% due to its multi-amine functionality. Adding NaOH in a 1:1 molar ratio with the amines boosted absorption by 5-10% across all temperatures studied. Statistical analysis revealed that amine concentration had the most significant impact on CO<sub>2</sub> absorption efficiency (p-value < 0.0001), followed by base concentration (p-value = 0.0014) and temperature (p-value < 0.0001). The ANOVA model ( $R^2 = 0.8733$ , Adj.  $R^2 = 0.8616$ ) effectively captured the variance in the data, although a significant lack of fit (p-value < 0.0001) suggested the need for further model refinement.

The calcium looping process using CaO as a sorbent demonstrated consistent cyclic CO<sub>2</sub> uptake of approximately 0.8 g CO<sub>2</sub>/g sorbent during the initial 10 cycles, corresponding to over 80% conversion of CaO to CaCO<sub>3</sub>. The cyclic working capacity remained stable for up to 25 cycles, after which a gradual decline was observed due to sorbent aging effects. The energy requirement for CaO regeneration via calcination was estimated at 3.5 GJ/tonne CO<sub>2</sub> captured, lower than typical amine-based capture systems.

While amine-based absorption systems offer rapid CO<sub>2</sub> capture kinetics, the significant energy requirement for solvent regeneration remains a key challenge. The calcium looping approach emerged as a promising alternative, with the advantage of fuel-free sorbent regeneration, provided that sorbent stability and reactivity can be maintained over numerous



cycles.

This research highlights the potential of optimized amine solutions and calcium looping as viable strategies for post-combustion CO<sub>2</sub> capture, contributing quantitative insights to promote sustainable practices in climate change mitigation. However, further research is necessary to address the limitations of each approach, including reduced energy requirements for amine systems and enhanced sorbent stability for calcium looping. Pilot-scale testing, techno-economic assessments, and environmental impact analyses will be crucial to pave the path for commercial deployment of these technologies.

#### **Disclosure of interest**

No potential competing interest was reported by the author(s).

#### **Declaration of funding**

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