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Carbonic Anhydrase Textile Structured Packing for Efficient CO_2 Absorption in Methyldiethanolamine Solvent

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Abstract

Carbonic anhydrase (CA) is an attractive biodegradable catalyst for CO_2 absorption in solvent-based CO_2 capture. However, maintaining the stability of CA as a homogeneous component of the solvents is a challenge. Solvent regeneration temperature typically exceeds the enzyme thermal tolerance, which leads to CA deactivation. To reduce the need for frequent CA replenishment and to avoid inactive CA accumulation in the solvent, this work shows the benefits of an immobilization strategy where CA is fixed in a second-generation design of textile structured packing (CATSP-2) modules. The enzyme-immobilized packing showed 1.5 times better performance in CO_2 separation compared to traditional structured packing with a corresponding increased CO_2 loading in the rich solvent. The modules exhibited good CA activity retention of ~80% during the tests without any CA replenishment. Applying CATSP-2 could potentially decrease the packing height and absorber column size for a lower cost per amount of CO_2 captured.

Key words: CO_2 capture; carbonic anhydrase; immobilization; packing; enzyme stability

Introduction

Post-combustion CO_2 capture by reactive absorption in solvents is one of the most promising technologies and closest to commercial scale for mitigating anthropogenic CO_2 emissions [1,2]. However, regenerating the solvent can require high energy cost, which is a major stumbling block to full-scale technology commercialization [3,4]. One possible method to address the high energy penalty is to shift the CO_2 absorption product from carbamates to bicarbonates/carbonates as these can be stripped out from solvent more readily with less energy consumption. This method also takes advantage of a larger theoretical absorption capacity in the solvent where generating one mole of bicarbonate consumes one mole of amine, in contrast with CO_2 absorption via carbamate formation, where the theoretical capacity is limited to 0.5 mole CO_2 per mole of amine due to the charge balance requirement. In this regard, tertiary amines have some advantages over common primary or secondary amines because tertiary amines absorb CO_2 through hydration leading to bicarbonate formation ($CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$). The downside of CO_2 absorption through hydration is the slower reaction rate compared to carbamate formation with primary and secondary amines. The second-order reaction rate constants of tertiary amines are typically a hundred times lower than the benchmark primary amine monoethanolamine (MEA) [5,6].

Carbonic anhydrase (CA) is an attractive reaction rate promoter for kinetically slower systems when assisted by sufficient alkalinity to promote proton shuttling [7]. This zinc metalloenzyme facilitates the efficient conversion of CO_2 to bicarbonate [8,9] until equilibrium is reached. Unlike other rate promoters that form covalent bonds with CO_2 directly, CA catalyzes the reaction between water and CO_2 in its catalytic "active site" without undergoing permanent chemical reaction. Many researchers have shown that the kinetics of CO_2 hydration in different

solvents can be significantly improved by introducing CA, which contributes to the mass transfer enhancement in CO_2 absorption [8,10,11]. Nevertheless, the application of soluble CA is hampered by its instability during thermal solvent regeneration. When homogeneously dissolved in the solvent, CA passes through the heat exchanger, stripper and reboiler of the carbon capture process. The high temperature in these process stages leads to fast deactivation of CA by denaturing ("unfolding"). Regular CA replenishment is therefore required to maintain efficient CO_2 absorption in homogeneous systems [12]. Generally speaking, constant replenishment of the CA does not generate economic benefit [13] and the accumulation of impurities will also cause operational problems, such as foaming, and require regular solvent filtering. As a solution, vacuum stripping has been employed to reduce the temperature required for solvent regeneration, down to 95 °C [12]. Comparing different rates of soluble CA replenishment found that 10% CA replenishment on a routine basis provided stable CO_2 capture performance. In those trials, after CA replenishment stopped, CO_2 absorption decreased by 30% in 67 hrs.

Immobilization is a known methodology to increase the stability and reusability of the enzyme catalysts. According to different immobilization principles, CA can be immobilized on solid surfaces through adsorption, surface covalent attachment, entrapment in polymers, or as cross-linked enzyme aggregates [14]. Much research has already focused on different CA immobilization strategies to intensify CO_2 absorption in slow kinetic solvents. Leimbrink et al., put granular CA in the pockets of structured packing for heterogeneous catalysis and found a minor improvement in absorption rate, though dissolved CA gave a significantly higher CO_2 absorption increase in a comparable set-up [15]. This is expected because catalyst in pockets is likely to have less exposed surface area, resulting in fewer opportunities to accelerate the reaction, than distributing catalyst over the packing surfaces. Zhang et al., immobilized CA on porous solid

support materials to increase the enzyme stability against high temperature and against typical flue gas contaminant compounds such as sulfate, nitrate and chloride [16]. Shao et al., used metal-organic frameworks and zeolitic imidazolate frameworks as candidate materials for enzyme immobilization and significantly improved enzyme stability in alkaline solution [17,18]. Rasouli et al., compared CA immobilization on packing surfaces versus immobilization on magnetic nanoparticles dispersed in the solvent. Results showed that both methods enhanced CA stability and CA was more catalytically effective when immobilized on magnetic nanoparticles due to less diffusion limitation [19]. However, the CO_2 capture system would face additional challenges in operation e.g., clogging and heat transfer efficiency decrease after introducing solid particles.

Immobilizing CA on the packing material for CO_2 reactive absorption in a conventional process configuration could prevent CA from exposure to the harsh stripping step. Conventional packing material is made of materials like steel, ceramic, or plastic. With conventional packing material and reactive solvents, CO_2 absorption occurs when gas flowing upward through the absorber column packing material encounters a chemically reactive solvent that spreads in a thin layer across the metal sheets or other packing surfaces as it flows downward over the packing by the force of gravity. The physical properties and geometry of the packings play a critical role in determining the location where CO_2 absorption happens. Solvent distribution needs to be carefully controlled to enable complete packing wetting, where "wetting" traditionally refers to the formation of a thin film of solvent across the entire packing surface. When CA is immobilized on solid packing surfaces, the dissolved CO_2 needs to transfer through the bulk liquid to the solid-liquid interface where CA is located to facilitate the CO_2 hydration reaction [20]. This means that when CA is immobilized on conventional packing surfaces, it can be more difficult for CA to perform its catalytic role because it will be not functional in dry areas or in locally flooded areas

where the liquid film is too thick.

Compared to the dissolution strategy – where CA is well dispersed in the solvent and is therefore present at the gas-liquid interface – the apparent catalytic effect of CA immobilized at a solid-liquid interface is generally expected to be lower due to mass transfer resistance caused by the need for CO_2 gas to diffuse through the solvent before reaching the enzyme. However, in other respects the immobilization strategy is more attractive than the dissolution strategy because CA can be retained in the absorber where it is stable and contributes catalytic benefit with significantly less replenishment demand. The key requirement is to fix CA appropriately by reducing diffusion limitation, offering good gas-liquid contact while also minimizing enzyme leaching, maintaining catalytic activity, and minimizing cost.

In our previous work, a robust biocatalytic yarn was developed that is not only easy to fabricate and handle but also able to provide excellent control of liquid flow within the yarns as conduits [21]. Subsequently, textile materials were fabricated into cylindrical-shaped drop-in-ready structured packings that provided efficient solvent distribution and gas-liquid-biocatalyst contact [22]. Biocatalytic surfaces were created on the textile packing modules by applying the naturally derived polymer chitosan as a stable thin coating on the textile cotton fibers. This coating served as an enzyme entrapment matrix with high activity retention and delivered superior performance in lab-scale CO_2 absorption tests using potassium carbonate solvent. Our second generation lab-scale biocatalytic textile structured packing [23] employed a crosslinking agent to chemically attach CAs on the surface of the textile fibers, both improving the longevity of the biocatalyst through covalent bonds and eliminating the mass transfer barrier associated with enzyme entrapment in the polymer matrix. This second-generation carbonic anhydrase textile structured packing (CATSP-2) was scaled up simply by increasing the total length of unassembled textile fabrics to adjust for the

increased number of spiral wraps. Several larger diameter packing modules were made to fit an integrated bench scale unit for testing under realistic post-combustion CO_2 capture conditions that would verify their ability to: 1) avoid frequent CA replenishment by preventing CA from entering the harsh desorber environment; and 2) maintain CA high catalytic effect for improving CO_2 absorption in a tertiary amine solvent. CO_2 absorption results using different testing scenarios of solvent and packing were compared to evaluate the performance of biocatalytic textile structured packing in a practical manner using an integrated absorption-desorption circulation system. Valuable information, including temperature profile, CO_2 capture rate and enzyme stability, was obtained that provides a basis for scaling up the technology for future use in post-combustion CO_2 capture and related CO_2 gas separation applications.

Experimental methods

Materials

CO_2 with purity of 99.9% and span gas with 14 vol % CO_2 were purchased from Scott-Gross Company, Inc. Phosphoric acid (≥ 85 wt%, Sigma-Aldrich) was used as received for CO_2 loading measurement and methyldiethanolamine (MDEA, ≥ 99%, Sigma-Aldrich) was diluted using de-ionized water. Experimental thermostable microbial carbonic anhydrase was obtained from Novozymes A/S (Bagsvaerd, Denmark) as a concentrated liquid solution and stored at –20 °C before use, referred to here as NZCA. To prepare homogeneous test solutions, the freshly thawed enzyme was extracted before dissolving into aqueous MDEA solvent. The textile structured packing was custom made at laboratory scale using polymer meshes, loose-weave cotton fabrics (chemically pure cellulose), and metal lath spacers (raised style with overlapping strands and diamond shaped openings of 1/2”×1/4”) to confer rigidity and adequate liquid and gas flow. The CATSP-2 module type made for bench unit testing was a larger diameter version of our previous

lab-scale prototypes [22,23], designed to perform at the higher and more realistic gas and liquid flow rates delivered through the integrated CO_2 capture system. Prior to integrated bench unit testing, all fabricated packings were test-fitted in a 76 mm column and were verified to be flooding-free in a pass-through flow test with maximum air flow rates of 120 L/min and water flow rate of 700 mL/min. Bare textile packing, with no chitosan coating, crosslinking or enzyme applied, was used as the no-CA blank (TSP-2). A one-pot surface-covalent immobilization method that created 3-D enzyme aggregates on the textile surfaces (to produce CATSP-2 type modules) was used for NZCA immobilization based on its high specific activity, high CO_2 capture efficiency, and long-term stability according to our lab-scale studies [23]. Briefly, pre-assembled textile packing was dip-coated with 1% chitosan dissolved in 5% acetic acid in a 2 L graduated cyclinder and air dried for 2 days. The dry chitosan-coated packing was immersed in 1.5 L phosphate buffered saline solution (pH 7.4) in a 2 L graduated cylinder with 2-inch magnetic stirrer operating at 200 RPM followed by addition of 140 U (esterase activity unit) of NZCA and 6 mL of 50% glutaraldehyde. Homogenous mixing was ensured by the observation of a vortex and the stirring was maintained for 18 hours at room temperature to promote crosslinking reactions. Then, the packing was rinsed thoroughly with water and immersed in 1.5 L of 25 mM Tris buffer for 4 hours with continuous stirring for 4 hours to cap the unreacted aldehyde. Finally, the enzyme immobilized packing was rinsed with water thoroughly and air dried. The average immobilized enzyme specific activity (esterase activity unit), calculated from samples cut from a freshly immobilized packing, was 0.38 U/g of cotton fabric. Similar to a reference 250Y Steel packing, each CATSP-2 packing module had a nominal diameter of 76 mm and a height of 228 mm (Figure 1). More comparisons with 250Y steel packing are shown in Table 1. Several modules were stacked to fill the required height in the absorption column, in the same manner as conventional structured packing.

Integrated bench scale CO_2 capture unit

The integrated bench scale CO_2 capture unit used for the packing test has been described in our previous work [24]. The unit includes a PVC transparent absorber column, a stainless-steel stripper column, and several heat exchangers to realize continuous CO_2 removal. The absorber column allows convenient packing switching for performance tests. The water saturated flue gas flow is fixed at 30 °C temperature with a 128 L/min total flow rate and a 14% CO_2 inlet concentration that simulates coal combustion flue gas entering at the bottom of the absorber column. Lean solvent that enters the top of the absorber column is set at 40 °C temperature with flow rates of 300, 500 and 700 mL/min. These liquid flow rates equate to 1.8, 3.4 and 4.3 liquid-to-gas (L/G, kg/kg) ratios in the absorber column. The CO_2 concentration of inlet and outlet gas is consistently monitored using Horiba VIA-510 gas analyzer, where the amount of CO_2 and N_2 into the absorber is controlled by mass flow controller to jointly obtain the CO_2 in and out mole flow rate. The data collected during the steady operation are averaged. The CO_2 absorption rate (r_{CO_2}, mol/s) is then calculated based on the inlet and outlet CO_2 mole flow rate in simulated gas and exhaust gas.

$$r_{CO_2} = n_{CO_2}^{in} - n_{CO_2}^{out} \quad (1)$$

where $n_{CO_2}^{in}$ is inlet CO_2 mole flow rate, mol/s; $n_{CO_2}^{out}$ is outlet CO_2 mole flow rate, mol/s.

A common tertiary amine, MDEA, was selected as the baseline CO_2 absorption solvent. Structured 250Y steel packing was used as the baseline [25,26]. Five testing campaigns were conducted as shown in Table 2 including: 1) MDEA solvent using 250Y steel packing; 2) NZCA dissolved in MDEA solvent using 250Y steel packing with NZCA added to achieve concentrations of between 0.5 and 3.5 g/L; 3) MDEA solvent using blank textile structured packing (TSP-2, no

enzyme); 4) MDEA solvent using NZCA immobilized biocatalytic textile structured packing (CATSP-2) modules; and 5) MDEA solvent using CATSP-2 with decreased packing height. For the dissolution and immobilization strategies, a comprehensive comparison was made of the temperature profiles in the absorber column, the overall CO_2 absorption rate (Table S1), and the effectiveness and stability of NZCA. Observed limitations and potential improvements are also discussed.

Solvent alkalinity, CO_2 loading and NZCA activity

Liquid samples were taken after the unit operating parameters reached a steady state. CO_2 loading in the amine solvent was obtained using a method where excess phosphoric acid released all CO_2 [24]. Alkalinity of the amine solvent was measured using an autotitrator (Metrohm 888 Titrando) with diluted sulfuric acid [27]. Dissolved NZCA activity retention in the solvent was measured by an adapted Wilbur-Anderson (W-A) assay [28], which uses dissolved CO_2 as the substrate. A 300x dilution in assay buffer was applied to the sampled solution and the no-enzyme solvent control to eliminate solvent effects during W-A assay tests. The NZCA used here is able to hydrolyze p-nitrophenylacetate (pNPAc) and release p-nitrophenol (pNP), making the activity of the immobilized NZCA in the solid state detectable by an esterase activity assay, which was used to evaluate activity retention of the immobilized NZCA on the biocatalytic textile packing after CO_2 absorption trials [22].

Results and discussion

CO_2 capture test w/o and w/ dissolved NZCA using structured packings

The initial tests in the bench-scale integrated CO_2 capture unit were carried out using 250Y steel packing and 30 wt% MDEA as the absorption solvent. After several tests were completed,

NZCA was dissolved in the MDEA solvent to evaluate the NZCA enhancement on CO_2 capture efficiency. The CO_2 absorption rates of Case 1 without NZCA and Case 2 with dissolved CA are summarized in Figure 2 and grouped based on different L/G ratios. Due to slight variations of alkalinity and CO_2 loading in the lean solvent, the concentration of free amine was normalized based on operating conditions, i.e. alkalinity, CO_2 loading and L/G ratio [24]. Results show that the CO_2 absorption rate increased with increasing free amine concentration and increasing L/G ratio for both Cases 1 and 2. Results confirm that the dissolved homogeneous NZCA is effective via sufficient interaction with CO_2 gas and alkaline bulk solvent for catalysis, increasing the kinetics of CO_2 hydration. Therefore, the mass transfer for CO_2 absorption was intensified, with a relative increase of CO_2 absorption rate by an average of 28% [22].

However, quick deactivation of NZCA occurred at high temperature as it passed through the stripper and NZCA activity dropped below the experimental limit of detection after continuous operation. This means frequent dissolved NZCA replenishment was required. Figure 3 shows the reboiler temperature profile and NZCA replenishment frequency during the Case 2 tests. A certain amount of solvent was replaced with fresh NZCA concentrated solvent for NZCA replenishment.

NZCA immobilization - packing CATSP-2

To counter the need for constant NZCA replenishment and other potential problems, NZCA was previously immobilized on the surface of a first generation textile structured packing through chitosan entrapment [22]. The entrapment immobilization strategy increases NZCA stability and reduces the enzyme requirement. However, the overall catalytic effects are expected to be lower due to increased mass transfer limitations due to the location of the enzyme buried in the matrix and performance could decline over time due to enzyme leaching, as has been observed for entrapment immobilization by other polymer matrix systems [29]. To address these issues, a second

generation biocatalytic textile structured packing was developed using a one-pot surface-covalent immobilization method. This method creates stable chemically crosslinked enzyme aggregates on the textiles surfaces which improves durability through covalent bonding and minimizes mass transfer barriers of the polymer immobilization matrix by exposing enzymes at the surface [23]. CATSP-2 prototypes also retained 100% and 85% of the initial CO_2 capture rate over extended 71-day longevity testing and after 1 year of ambient dry storage, respectively [23]. The textile structured packing was scaled-up by increasing the diameter of the packing to 76 mm to fit snuggly in the absorber column of the integrated bench scale unit and metal spacers with raised overlapping strands were added to improve rigidity and accommodate higher liquid and gas flow rates. All fabricated packings were flooding-free in a mock flow test with maximum air flow rate of 120 L/min and water flow rate of 700 mL/min. Each biocatalytic textile structured packing had a height of 228 mm and 8 packings were stacked and worked together in the absorption column of the bench CO_2 capture system.

CO_2 capture tests of CA-immobilized packing

To make a comprehensive evaluation on the immobilization strategy, CATSP-2 modules were tested in the integrated bench scale unit using MDEA solvent. Because textile structured packing has different mass transfer and hydraulic characteristics from 250Y steel packing in terms of mass transfer coefficient, pressure drop, liquid holdup and interfacial area, a bare textile structured packing (TSP-2) without NZCA immobilization was used for comparison. The choice of using bare TSP-2 packing as a "blank" reference for these tests, rather than chitosan-coated TSP-2, was because the bare and chitosan-coated TSP-2 performed similarly in lab scale tests, at 4 L min^{-1} gas flow rate, and using the bare TSP-2 would provide information on the CO_2 capture efficiency of the unmodified textile.

Absorber temperature profile

Since CO_2 absorption in MDEA is exothermic, higher CO_2 absorption usually means more heat release. Measuring the temperature profile along the absorber column is a convenient way to quickly evaluate the solvent kinetic performance. Several thermocouples were distributed evenly along the absorber column. The temperature profiles observed for Cases 3 and 4 are presented in Table 3. Thermocouple TC-1 measured temperature at the top of CATSP-2 packing. Thus, the temperature of TC-1 was close to 40 °C, which was the solvent feeding temperature. TC-2 and TC-3 measured the temperature in the middle and bottom of the absorber column. Unlike primary or secondary amines, the CO_2 absorption heat of tertiary amines is smaller and a temperature bulge may not occur in the absorber column due to slower reaction kinetics, even though the absorption is an exothermic process [30]. Since the solvent inlet temperature was higher than the ambient temperature, the solvent temperature would only show a decreasing trend as it flowed down the column due to a cooling effect of the countercurrent flowing flue gas. The feed gas temperature was around 30 °C. Comparing the temperature profiles between Cases 3 and 4 below TC-1, there is a steeper temperature decrease in Case 3, indicating less CO_2 absorption, while the temperature decreases in a slower manner in Case 4, meaning additional CO_2 capture occurred due to the CATSP-2 packing. NZCA especially helps in catalyzing the reaction when the CO_2 loading in solvent is higher and inherent kinetics slow down. Similar phenomena were observed at all three L/G levels.

CO_2 absorption rate

The CO_2 absorption rate of Cases 3 and 4 are summarized in Figure 4 to show that the rate is higher in Case 4. There is a relative 12% increase in CO_2 absorption rate under all three L/G ratios. This indicates that CO_2 absorption is intensified by the presence of immobilized NZCA in

CATSP-2 packings. Although the relative percentage increase is smaller than that observed in the dissolution strategy, this could partially be because the CO_2 absorption rate in Case 3 is higher than that in Case 1, i.e. the blank TSP-2 itself demonstrates a higher gas separation efficiency than 250 Y steel packing. If the comparison is made by the absolute difference of absorption rate, NZCA effectiveness in enhancing mass transfer by the immobilization strategy is 81.7% of that based on the dissolution strategy. As mentioned before, NZCA has better dispersion and catalytic effect when dissolved in the solvent versus when CO_2 needs to transfer through the bulk liquid to reach NZCA immobilized on solid surfaces. However, the solid surfaces of textile structured packing made using cotton and chitosan-coated cotton with immobilized enzyme are distinctly different from steel surfaces because, while steel does not absorb water at all, cotton yarns are hydrophilic and readily absorb water deep into their structure. This means that at certain flow rates, solvent flows primarily within the yarns rather than at the yarn surfaces [21]. At such flow rates, the liquid film on the packing surface will be thinner which will shorten the distance between NZCA and gas-liquid interface (Figure 5) for less diffusion resistance and more rapid contact between CO_2 molecules and NZCA due to turbulence at the interface. The catalytic effect on CO_2 hydration can therefore be maximized. However, it also means that when the rate of liquid flow exceeds the absorption capacity of the textile, local flooding could occur in which the liquid layer around the textile surface increases, creating a thicker liquid layer that hinders the benefit of textile packing. In addition, there could be an excessive liquid holdup with a certain portion of solvent retained inside the packing that has limited contribution in CO_2 absorption. Observations that CO_2 absorption rates showed a downward trend with increased flow rate of free amine are attributed to this effect. Although higher liquid circulation rate increased the free amine concentration in the absorber column, the CO_2 loading in lean solvent also increased with liquid circulation rate due to

physical limitations of our integrated bench scale unit. If the packing fails to provide appropriate gas-liquid contact at the absorber column bottom under high liquid circulation rate, the weaker driving force could lead to a drop-in CO_2 absorption rate. Consequently, the highest CO_2 absorption rate, observed at 1.8 L/G for CATSP-2 packings was attributed to this condition providing the best gas-liquid-biocatalyst contact. We expect that improved textile packing designs could minimize excess liquid hold-up at high liquid flow rates. Nevertheless, a comparison of Figure 4 and Figure 2 shows that even at the highest L/G, the CO_2 absorption rate by CATSP-2 (~1.8 mmol s^{-1}) was greater than the best performing 250Y with dissolved CA (~1.25 mmol s^{-1}).

Stability of immobilized NZCA

The stability of immobilized NZCA is critical information in the development of CATSP-2 packing. The CO_2 absorption rate over the whole experimental period for Case 4 is shown in Figure 6. No enzyme replenishment occurred during the tests in Case 4, only the original immobilized NZCA was present throughout the Case 4 testing. Results show that in the last three hours of steady operation, the CO_2 absorption rate still maintained as high a level as the initial performance. Note that Figure 6 only shows data acquired close to the steady operation of a particular trial – the warming up, pre-steady, cooling and shut down processes are excluded from the data summary. Therefore, the actual operating time for which immobilized NZCA stayed in the system was much longer than depicted in Figure 6. In contrast, the dissolution strategy required regular NZCA replenishment. Our previous work showed a rapid CO_2 absorption decrease without NZCA replenishment [12]. These results prove that CA performance stability was greatly improved via the immobilization strategy in CATSP-2 packings. While some degree of foaming was observed for the CATSP-2 packing, which may be due to the composition of packing materials as well the porosity of the packing, application of antifoam resolved the foaming issue.

To further study the enzyme stability in dissolution and immobilization strategies, NZCA activity in Cases 2 and 4 were also evaluated before and after the CO_2 absorption test. In Case 2, a sample of circulated solvent with dissolved NZCA was taken before the unit heated up. The solvent showed high NZCA activity retention of 81.6% compared to freshly thawed NZCA product. This means that CA was relatively stable in 30 wt% MDEA solvent. However, after continuously passing through the high temperature reboiler, preheater and heat exchanger, the NZCA activity in the solvent dropped below the limit of detection (Table S2). Therefore, activity loss in the used solvent was largely attributed to NZCA deactivation at high temperature. From Case 4, two post-testing CATSP-2 modules were rinsed, air-dried, dissembled, and cut to take samples evenly over the surface of the whole packings. The average pNP release rates for the two modules were 2.82 and 2.66 nmol/min. The average pNP release rate of freshly made NZCA-immobilized textile structured packings was 3.48 nmol/min. Therefore, the immobilization strategy successfully retained high NZCA activity (81% and 76%) after the 1600 minutes tests in the absorption-desorption integrated circulation system.

Cases comparison with short absorber column (Case 5)

Case 5 was tested with decreased packing height. The bottom three CATSP-2 packings were removed compared with Case 4, leaving five CATSP-2 packings and 1140 mm (~37% less) total packing height. All cases were compared together in terms of the average CO_2 absorption rate and the rate was converted to an improvement factor using Case 1 as the baseline (Figure 7). The Case 2 dissolution strategy shows about 1.3 performance improvement in CO_2 absorption. Case 3, with blank TSP-2 packing, shows a dramatically higher improvement factor from 2.3 to 1.7 depending on the L/G ratio. Since the reaction kinetics are the same in Cases 1 and 3, the improvement is likely due to a larger liquid holdup and better gas-liquid distribution in Case 3, where hydrophilic

absorbent textile packing would naturally retain more solvent than non-absorbent steel packing. Larger liquid hold-up means there is more unreacted amine in the absorber column for Case 3 CO_2 absorption at the same packing height as Case 1. When NZCA is immobilized for catalysis (Case 4), the performance further improves with maximum 2.5 improvement factor at 1.8 L/G, indicating a combined benefit of textile packing and NZCA catalysis. The unique flow pattern within the yarn of textile packing and higher liquid hold-up could give immobilized NZCA more opportunities for catalyzing the CO_2 hydration reactions. The immobilized NZCA also maintains a favorable catalytic performance over time in contrast to the situation where NZCA is dissolved in the solvent (Case 2). Although the CATSP-2 packing height is decreased by 37% in Case 5, this case still shows 2.1 improvement factor over Case 1 at 1.8 L/G. All the results show that both the TSP-2 and CATSP-2 packings have better performance at low L/G ratio, namely a lower liquid circulation rate.

Conclusions

This work studied CA dissolution and immobilization strategies for enhancing reaction kinetics and mass transfer in CO_2 absorption. A 30% increase in absorption efficiency was observed when NZCA was dissolved in the MDEA solvent, indicating that dissolved NZCA with good catalyst dispersion provided excellent catalytic effectiveness in the integrated bench scale CO_2 capture unit. However, deactivation issues arose because NZCA could not tolerate continuously passing through hot spots in the CO_2 capture system. Frequent NZCA replenishment was required to maintain the catalytic effect, making this approach less practical.

A one-pot surface covalent attachment method was used to immobilize NZCA on the fiber surfaces of textile structured packing. The absorbent textile material enabled higher solvent retention than traditional stainless-steel packing, which was considered beneficial for improving

the catalytic effect of immobilized CA. The Case 4 CATSP-2 packing showed maximum 2.5 improvement factor compared to the Case 1 baseline. The improvement was sustainable during the testing period, confirming the stability of CATSP-2 packing. With only a slight sacrifice of NZCA effectiveness, NZCA was retained in the absorber and avoided entering the harsh stripper environment in the system. Immobilized NZCA retained 76% to 81% activity after the test, which is promising for further development. A decreased packing height was applied in Case 5 for comparison. The capture efficiency indicates Case 5 is better than Case 2 but slightly worse than Case 3. Overall, the results revealed the potential of CATSP-2 packing to reduce absorber column size and capital cost. However, some operational issues were encountered with CATSP-2 packing. Some degree of foaming was observed which may be due to residual chemicals that were not completely washed away during fabrication of this prototype CATSP-2 packing. The foaming was mitigated using common antifoam. In addition, greater solvent retention, namely liquid load in the absorber means higher solvent inventory and corresponding cost, though this could potentially be offset by reducing the packing height, combining different packing materials, or by other packing and process modifications, such as co-current flow to aid liquid spreading and rate of solvent flow through the packing. The solvent retention rate needs to be optimized to balance the solvent usage and catalyst functionality. Future work would advance the packing design and process configuration to address these issues for easy operation and scale-up of the CO_2 capture system.

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Data Availability and Reproducibility Statement

The numerical data from Figures 2, 4 and 7 are tabulated in the Table S1 of Supplementary Material. The numerical data from Figures 3, and 6 are available in the Supplementary Material 2.

Figure captions

Figure 1. Schematic diagram of 250Y Steel packing (a) and CATSP-2 packing (b) for CO_2 absorption.

Figure 2. Comparing CO_2 absorption rate between Cases 1 (w/o CA) and 2 (w/ CA).

Figure 3. CO_2 absorption over the cumulative time in the integrated CO_2 capture unit for Case 2.

Figure 4. Comparing CO_2 absorption rate between Cases 3 (blank TSP-2 packing) and 4 (CA immobilized CATSP-2 packing).

Figure 5. Generic schematic diagram of gas-liquid contact in metal and CATSP-2 packings (liquid film thickness: $\delta_1 > \delta_2$). In a conventional packed column, the packing is oriented vertically, and the liquid flows downward by the force of gravity.

Figure 6. CO_2 absorption over the cumulative time in the integrated CO_2 capture unit for Cases 1 and 4. The warming up, pre-steady and shut down time are excluded from the data as they are not used in the calculation.

Figure 7. Improvement factor over Case 1. All experiments were conducted at the same conditions in terms of inlet CO_2 concentration (14%), temperature (40 ℃) and CO_2 loading (0.09 $C \cdot N^{-1}$) in lean solvent. NZCA biocatalyst was dissolved in MDEA solution for Case 2 and immobilized on CATSP-2 packing for Cases 4 and 5.

Table Captions

Table 1. Comparison of different cases tested in the integrated CO_2 capture unit

Table 2. Comparison of different cases tested in the integrated CO_2 capture unit where the dissolved NZCA concecentration is between 0.5 and 3.5 g/L

Table 3. Temperature of absorber column where TC-1, TC-2 and TC-3 locates at the top, middle and bottom of the packings

Table 1. Comparison of different cases tested in the integrated CO_2 capture unit

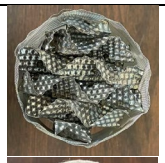
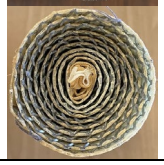
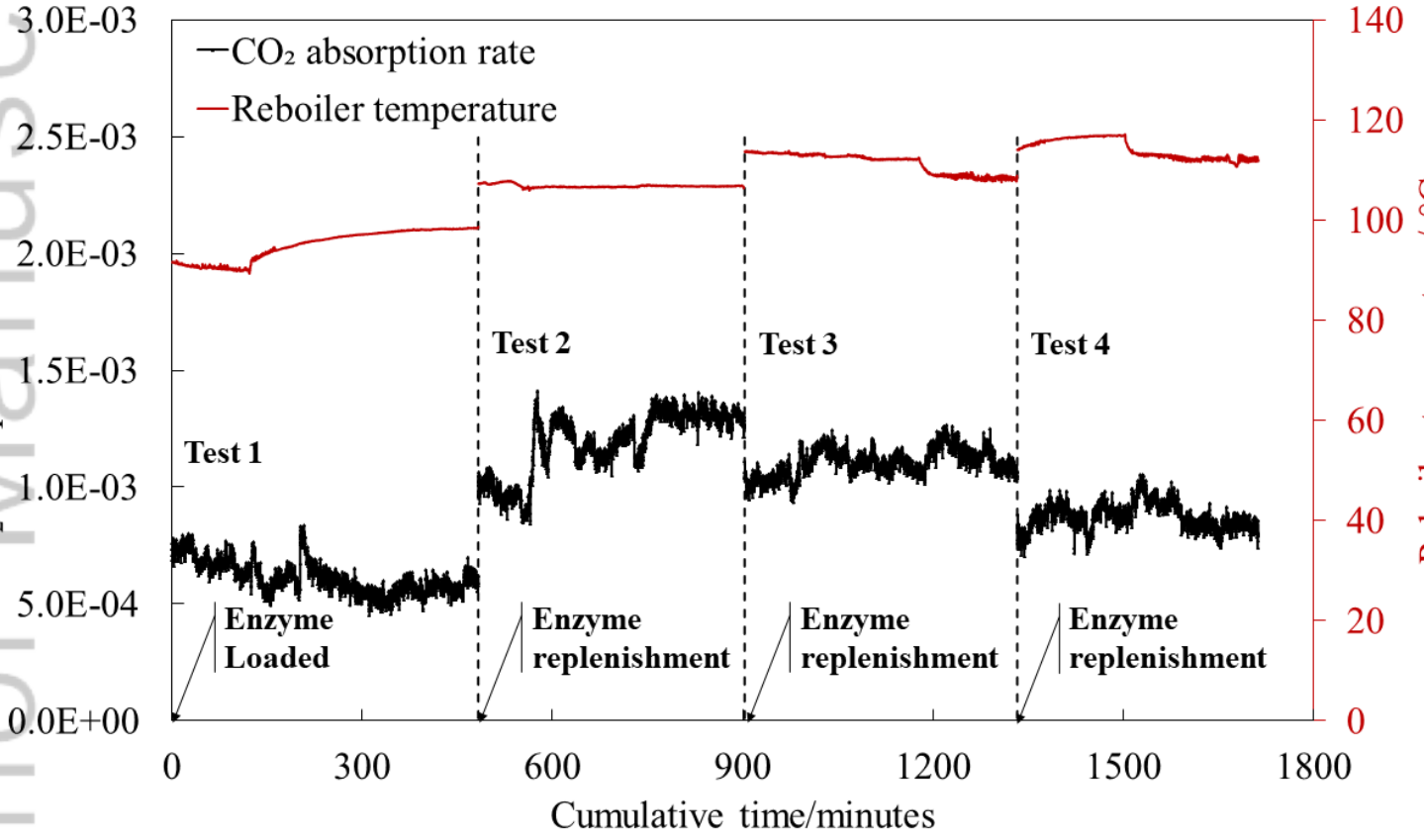
Packing	Height × diameter (mm)	Material	Enzyme immobilized	Top view	Side view
250Y Steel	152 × 76	Stainless steel	×		
TSP-2	228 × 76	Cotton fibers and spacer	×		
CATSP-2	228 × 76	Cotton fibers and spacer	✓		

Table 2. Comparison of different cases tested in the integrated CO_2 capture unit where the dissolved NZCA concecentration is between 0.5 and 3.5 g/L

Case	Solvent	Packing	Total packing height, mm
1	30 wt% MDEA	250Y Steel	1824
2	30 wt% MDEA + dissolved enzyme	250Y Steel	1824
3	30 wt% MDEA	TSP-2	1824
4	30 wt% MDEA	CATSP-2	1824
5	30 wt% MDEA	CATSP-2	1140

Table 3. Temperature of absorber column where TC-1, TC-2 and TC-3 locates at the top, middle and bottom of the packings

	L/G, kg/kg	TC-1, °C	TC-2, °C	TC-3, °C
Case 3	1.8	40.1	38.4	37.6
	3.4	40.1	39.4	39.0
	4.3	40.1	39.8	39.5
Case 4	1.8	40.3	40.2	39.6
	3.4	40.1	40.1	39.7
	4.3	40.0	40.1	39.8



Fgiure 3.TIF

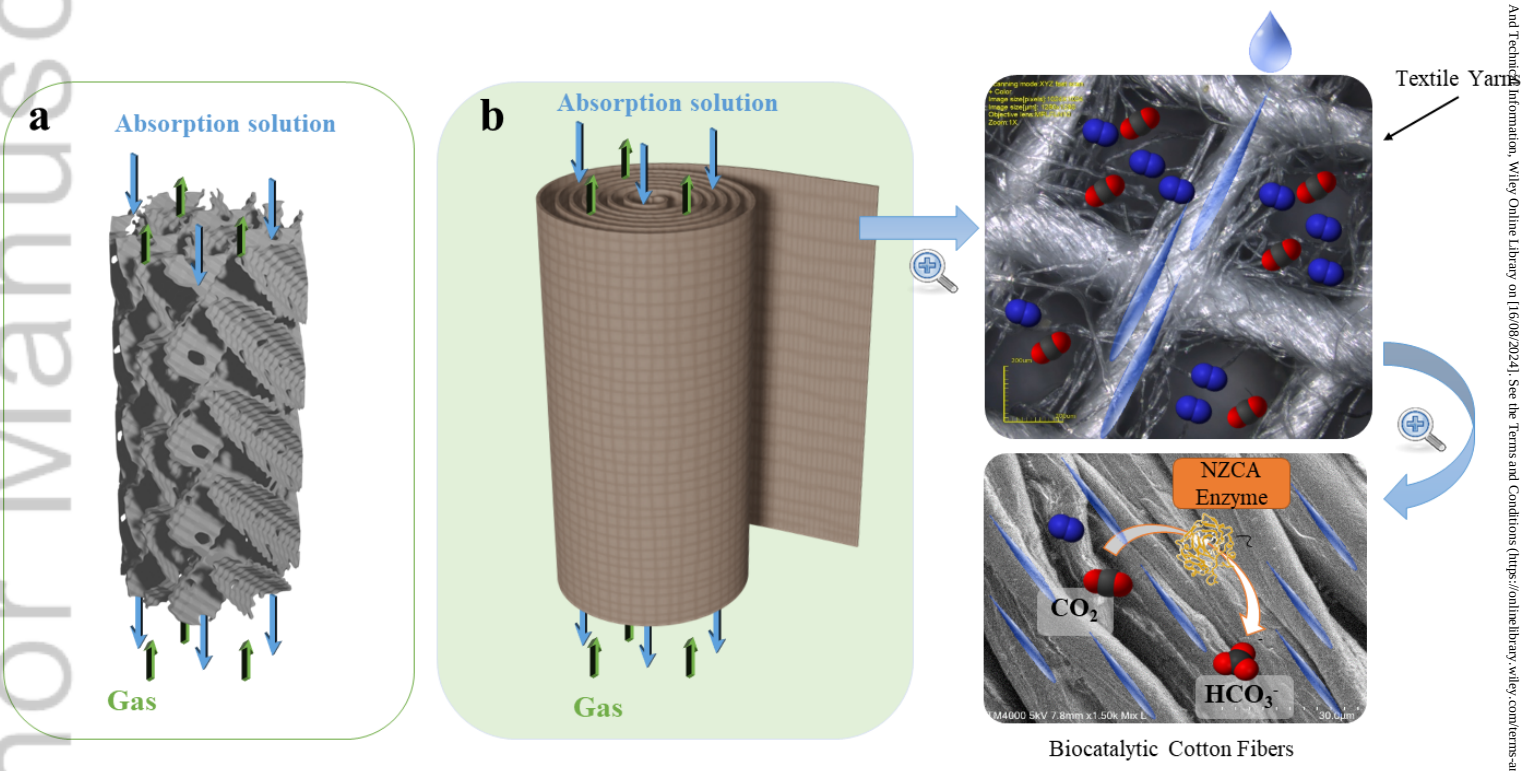


Figure 1.TIF

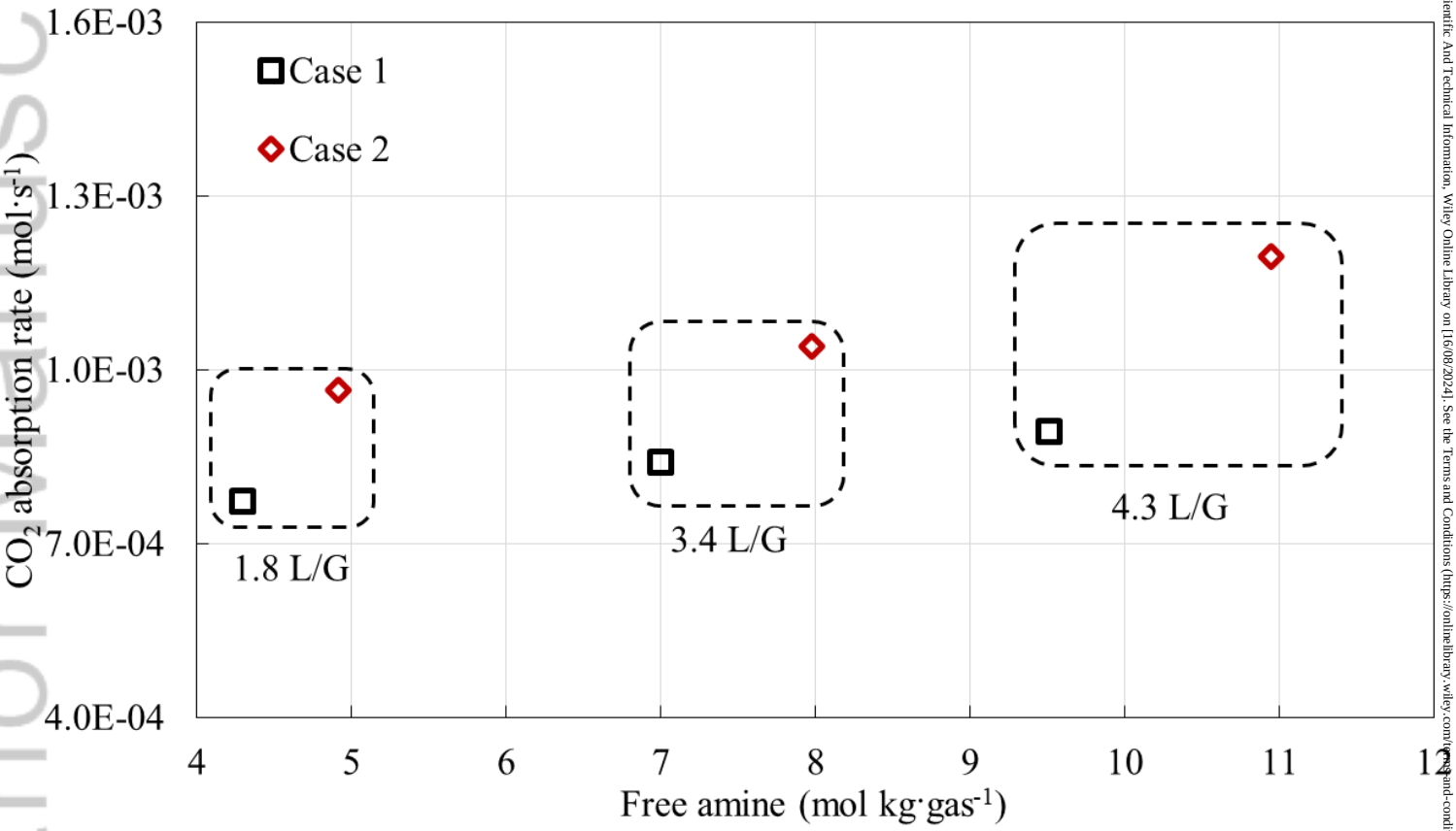


Figure 2.TIF

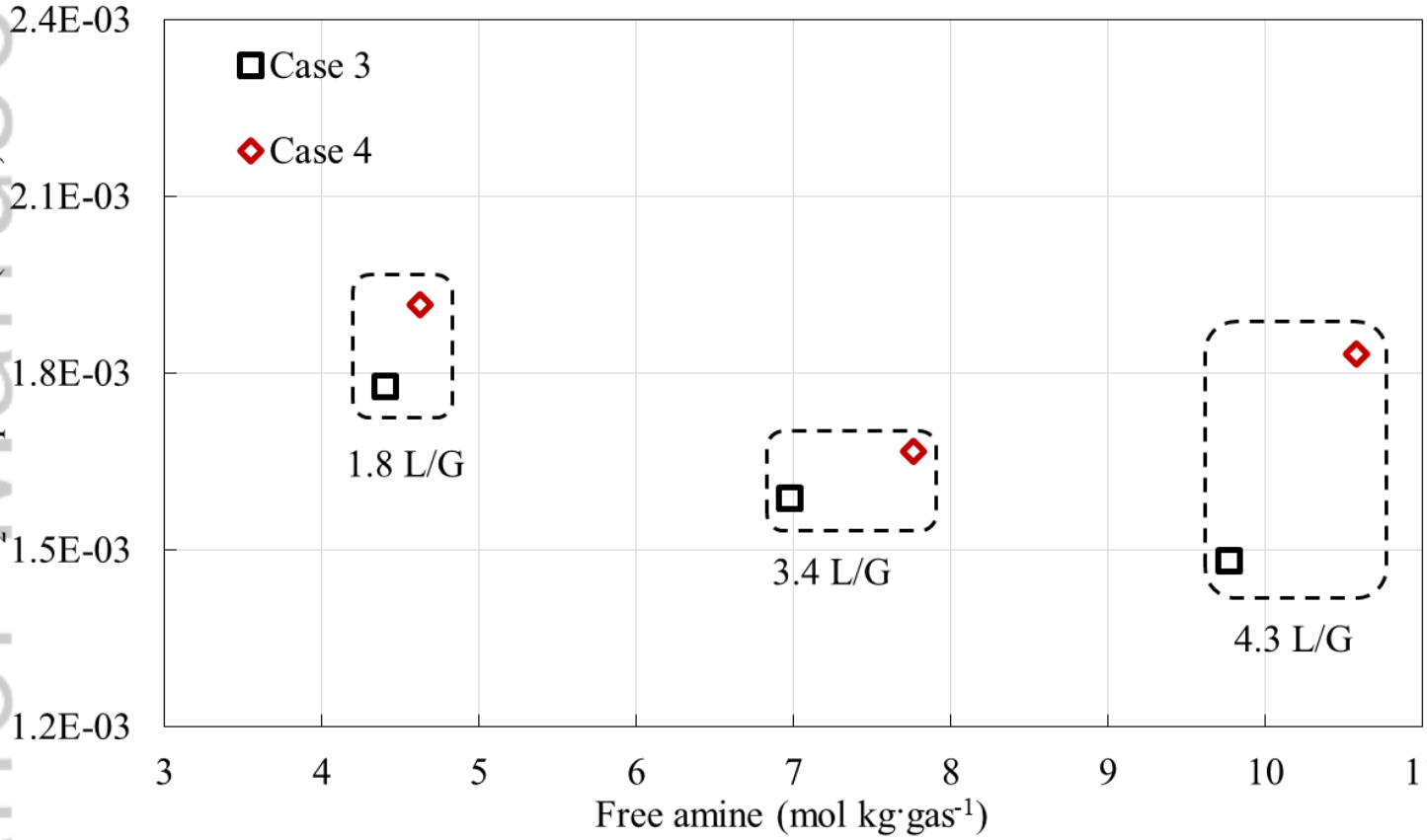


Figure 4.TIF

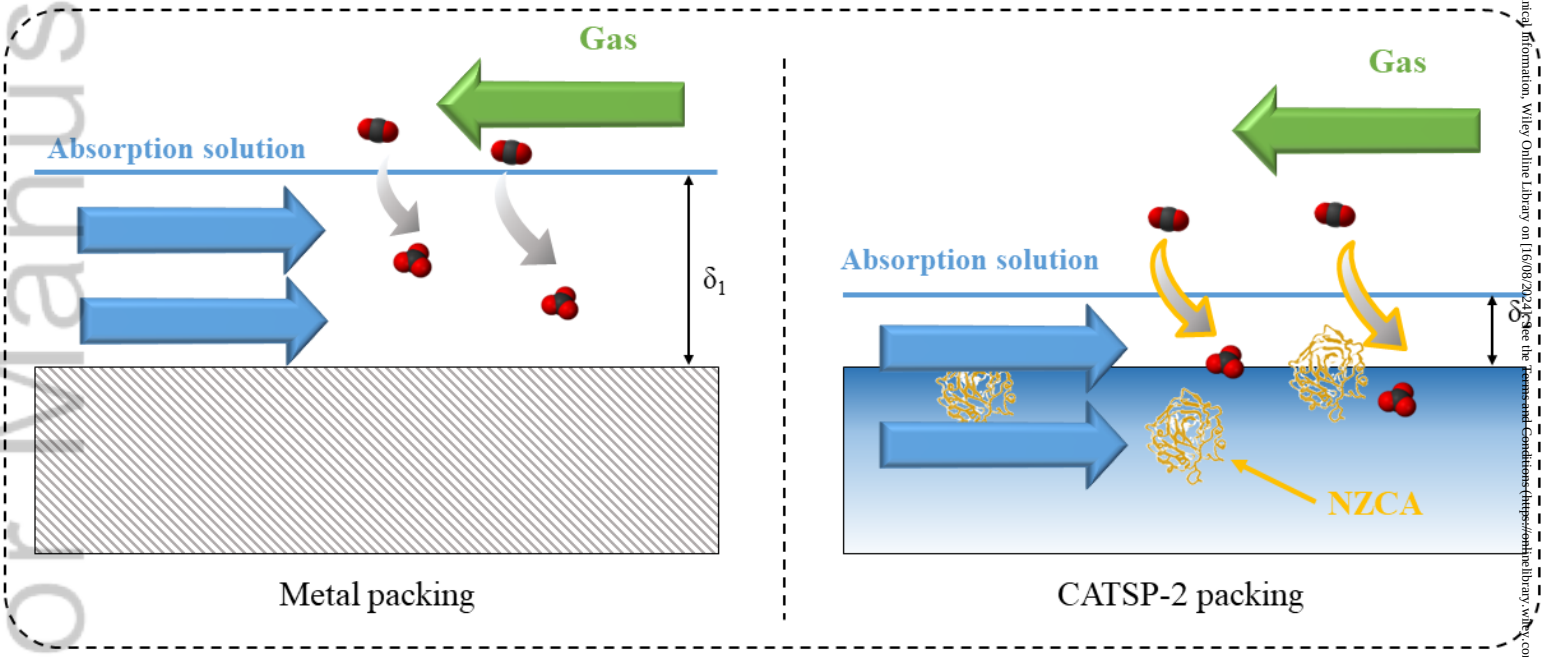


Figure 5.TIF

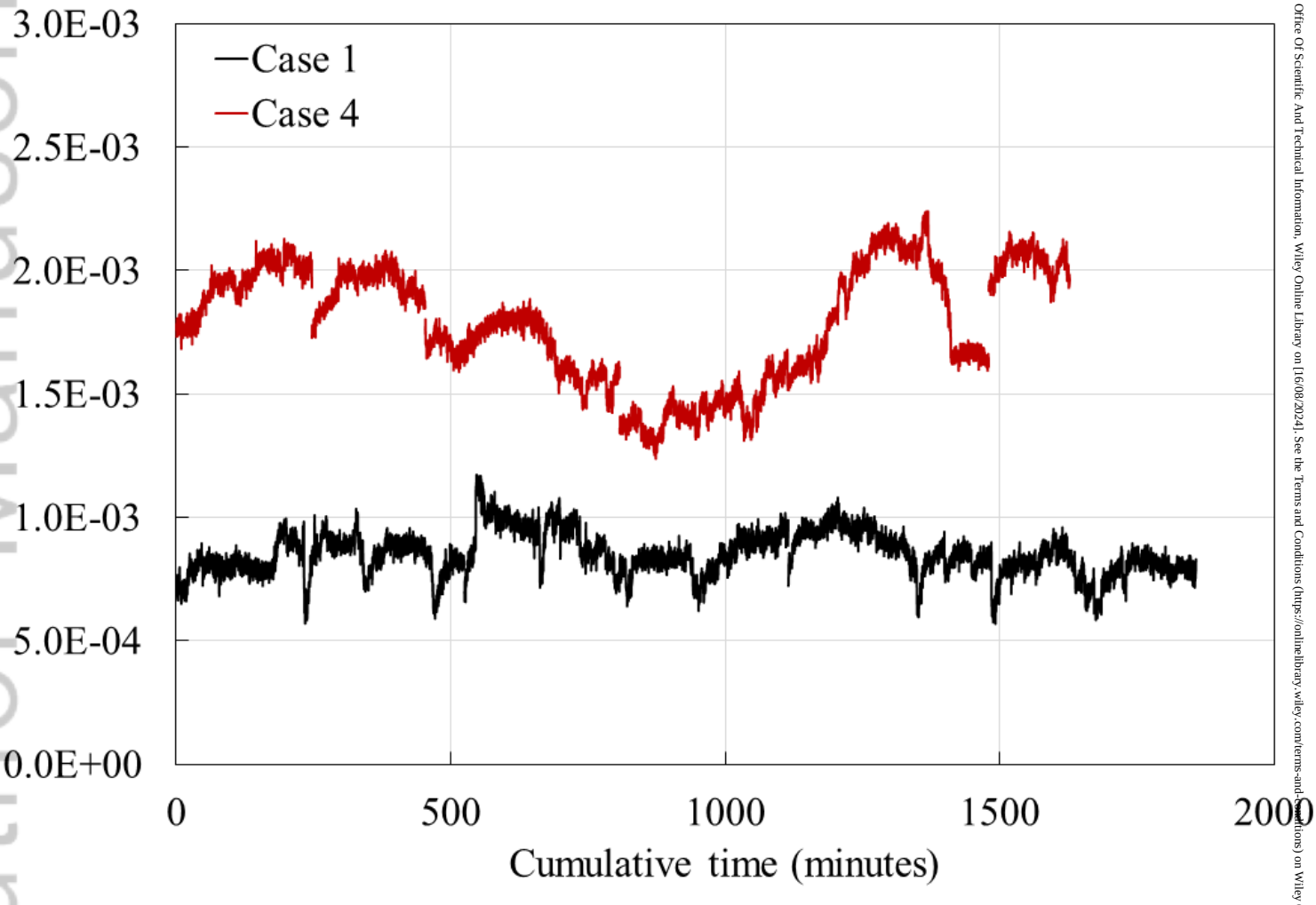
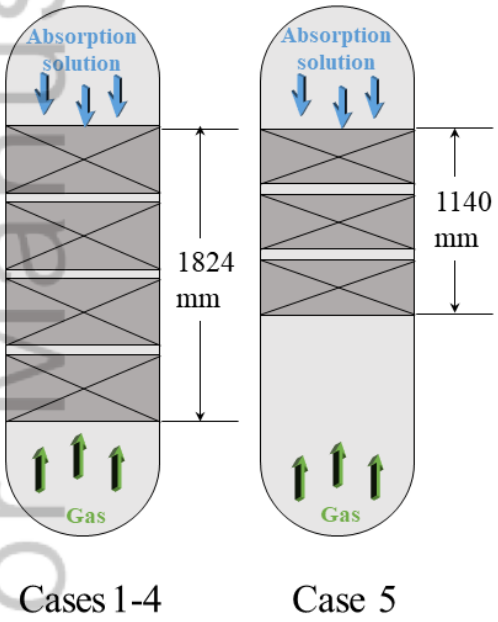


Figure 6.TIF



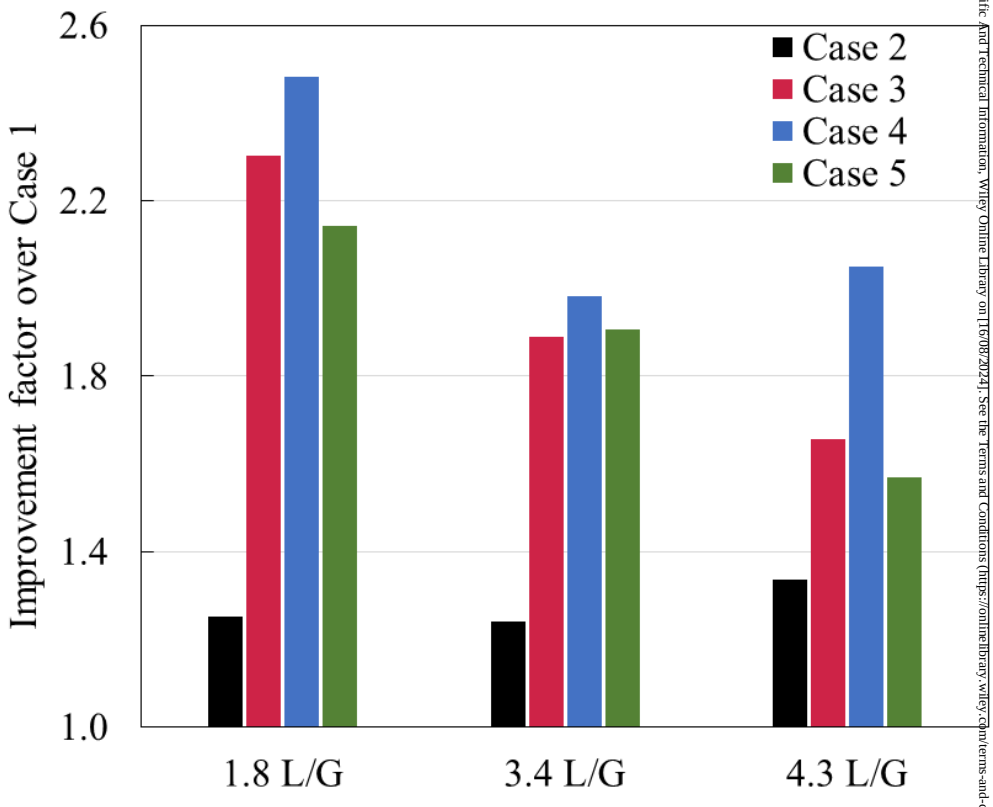


Figure 7.TIF

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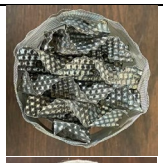
250Y Steel	152 × 76	Stainless steel	×		
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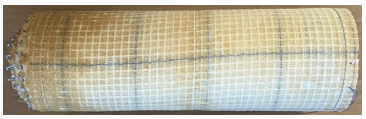
CATSP-2	228 × 76	Cotton fibers and spacer	✓		

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	4.3	40.0	40.1	39.8