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An adsorption-based CO₂ treatment unit for ultra-low fresh air HVAC system using solid amine

Yiyi Chu^a, Peng Xu^{b,*}, Yunfei Jia^b, Meishun Lin^c, Cheng Peng^c, Qiang Dou^c

^a College of Civil Engineering, Michigan State University, East Lansing, MI 48823, USA
^b School of Mechanical Engineering, Tongji University, Shanghai 201804, China

^c Persagy Technology Co., Ltd, Beijing 100096, China

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ABSTRACT

Fresh air load is an important factor in reducing overall building energy load as the building envelope insulation and various passive building technologies develop. A large amount of fresh air is needed to meet the high requirement of indoor hygiene and air quality. Although various energy-efficient technologies have been studied to reduce fresh air load, the energy savings are limited to only cold climate conditions. Traditionally, outdoor air is introduced to dilute indoor pollutants. In this paper, a novel independent CO₂ treatment unit (CTU) with the solid amine adsorbent (HP2MGL-PEI (600)-50) was investigated, which uses pollutant purification method instead of the conventional ventilation-based method to remove CO₂. Experimental investigation and robust theoretical energy simulations were carried out to validate the effectiveness and practicability of this unit and to evaluate the energy savings in real buildings. Experimental results show the CTU could effectively reduce the CO₂ concentration under normal atmospheric conditions in real buildings. Specifically, the adsorbent has a better adsorption performance with lower air velocity, but air velocity had a slight influence on desorption performance. The temperature has significant effects on both adsorption and desorption properties. An increment in adsorbent volume could also improve the adsorption performance. Simulations show that the indoor CO₂ concentration could be always controlled below 1000 ppm under proper control strategies. Thus, the amount of required fresh air could be dramatically decreased. The amount of energy savings of the reference building was approximately 13.18%. The static payback time of this new system was approximately 6.85 years.

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1. Introduction

Introducing fresh air in air-conditioning systems is the key point to ensuring favorable indoor air quality. However, the energy consumption of the fresh air inlet accounts for approximately 25– 30% of the total energy usage in heating, ventilating, and airconditioning (HVAC) systems, and even up to 40% in top-notch hotels and commercial buildings [1]. As global climate changes and low-carbon consciousness advances, ultra-low-energy buildings, passive buildings, and zero-energy buildings have been studied extensively worldwide. The insulation and overall air tightness of passive buildings and zero-energy buildings are greatly improved; thus, the heat conduction from the envelope and the cooling/heating loss caused by air infiltration are effectively

* Corresponding author. E-mail address: xupeng@tongji.edu.cn (P. Xu). reduced. However, fresh air is important to meet the requirement of indoor hygiene and ventilation, and the energy consumption for fresh air treatment and distribution is still high. The proportion of fresh air load, as a result, is significant in modern buildings. Therefore, the fresh air load has high potential for energy savings in HVAC systems.

Carbon dioxide (CO₂) was previously used as an indicator to calculate the fresh air volume required for the indoor environment. Nonetheless, latest researches demonstrated that the increase in CO₂ concentration will bring adverse effects to human behavioral ability. For example, compared to 600 ppm, the behavioral capacity of humans exposed to 1000 ppm and 2500 ppm decreased by 6/9 and 7/9, respectively [2]. Du et al. [3] reported that the elevated CO₂ concentration sometimes found to significantly impair cognitive function and work/school performance. For this reason, CO₂ currently has been considered as a nonnegligible contaminant in indoor environment,







especially in some confined spaces such as aircrafts and submarines where CO₂ treatment is essential. Traditionally, indoor CO₂ is diluted by fresh air, of which the demand-controlled ventilation strategy is one popular way to reduce the fresh air load based on real time indoor CO₂ concentration. For example, Lu et al. [4] proposed a dynamic control strategy which calculates ventilation rate dynamically by solving the CO₂ mass balance equation to keep indoor CO₂ near the set point during the occupied period. ASHRAE 62.1 [5] and ASHRAE Guideline 36 [6] also provide ventilation-based control to save energy, including occupant-based control and CO2-based control. Occupant-based control is mainly used in commercial buildings where ventilation rate can be adjusted based on the actual number of occupants. And CO₂-based control generally works with CO₂ sensors to control indoor CO₂ concentration at an acceptable level. However, these ventilation-based control strategies still require the HVAC system to introduce enough fresh air to maintain indoor air quality. Thus, their effect on energy savings is still limited.

Besides CO₂, volatile organic compounds (VOCs) represented by formaldehyde are also ubiquitous indoor pollutants which are irritants and are harmful to human health. Xiao et al. [7] developed an air purifier with activated carbon as regenerable adsorbent to remove indoor formaldehyde. It was found that the adsorbent had no damage after 5 cycles of adsorptionregeneration, but it lacked further studies on the effects of environmental conditions such as temperature and humidity on purifier performance. Tang et al. [8] tested the performance of an air purifier with polyamine-coated silica as an adsorbent under various factors such as environmental conditions and adsorbent aging. Results show that while reducing indoor CO₂ concentration, the system was promising in scrubbing formaldehyde from indoor air, justifying the effectiveness of aminefunctionalized materials and in-situ thermally regenerated systems in indoor air cleaning. The same authors also found that although formaldehyde accumulated in large quantities in the adsorbent, it was far from reaching saturation. Moreover, Nomura and Iones [9] as well as Ewlad-Ahmed et al. [10] reported that the release of adsorbed formaldehyde from amines is unlikely. Therefore, VOCs can be removed along with absorbing CO₂, but because of their low concentration, we still adopt CO₂ concentration as an indicator of indoor air quality. Additionally, none of the above studies paid attention to the rational selection of adsorbent materials and the energy consumption of adsorption systems in real-world scenarios which are the main concerns of the present study.

In this study, an innovative ultra-low fresh air HVAC system was introduced that could refresh the indoor air with limited outdoor air. A novel independent CO₂ treatment unit (CTU) with the solid amine adsorbent (HP2MGL-PEI (600)-50) was designed and investigated by using pollutant purification method instead of the conventional ventilation-based method to remove CO2. At first, Section 2 reviews existing CO₂ capture materials and methods. Section 3 provides detailed information about why HP2MGL-PEI (600)-50 was selected as the adsorbent material and how the structure of CTU was decided for this study. After that, Section 4 discusses about the experimental investigation to evaluate the performance of the adsorbent material and to verify the feasibility and efficiency of the CTU. At last, Section 5 introduces the theoretical simulations to verify the energy savings of the ultra-low fresh air HVAC system as well as the economic analysis to estimate the static payback time of this system. The framework for this study is summarized in Fig. 1. Other indoor contaminants, such as VOCs and particulate matter, are not discussed in this study.

2. Review of CO₂ capture materials, methods and systems

2.1. CO₂ capture materials and methods

Absorption, adsorption [11], membrane separation [12], cryogenic separation [13], and chemical distillation [14] are commonly used methods for CO_2 adsorption and desorption. Depending on the operating conditions, adsorption and desorption could be realized by one or several methods combined [15]. The summary of the various CO_2 capture materials and methods is shown in Table 1.

Cryogenics is widely used for the separation of nitrogen (N₂) and oxygen (O₂); however, it is impractical for large-scale CO₂ adsorption/desorption because of its high energy consumption. Membrane separation is more suitable for high CO₂ concentrations [16,17], such as fumes in coal-fired power plants. Alcohol, polyethylene glycol, and other oxidizing compounds are commonly used as physical adsorbents to absorb and desorb acidic gases, such as CO₂ and H₂S, but these physical adsorbents generally require CO₂ desorption at high pressures. The adsorption/desorption system based on aqueous solutions of amines [18] is the most extensive method for high concentration CO₂ capture in the flue gas of coal burning power plants. However, using these relatively welldeveloped amine solutions requires high energy consumption for CO₂ adsorption, along with corrosion and amine degradation issues, which are the main drawbacks in the application of amine solutions. Ionic liquids have some merits, such as low steam partial pressure, and their ionic group contains special functions such as amine groups, which are also beneficial to CO₂ adsorbent. However, the preparation and purification of these specific functional ionic groups are usually very demanding and costly.

Owing to the weaknesses of aqueous solutions of amines in adsorption, many scholars focus their attention to solid adsorbents, of which amine and polyamine are either physically or chemically bonded on a support such as silica gel, alumina, activated carbon, zeolite, and iron oxide framework. Physical adsorbents have shown good CO₂ adsorption performance at lower temperatures, like molecular sieve and activated carbon [7,19], metal-organic frameworks [20], and zeolitic imidazolate frameworks [21]. However, the adsorption capacity decreases considerably with increasing adsorption temperature. Furthermore, the challenge is the low separation coefficient of these physical solid adsorbents toward CO₂, which makes them inapplicable for adsorption or desorption at low CO₂ concentration. Moreover, the adsorption capacity of such solid adsorbents decreases significantly in the presence of water molecules; thus, dehydration is necessary before CO₂ adsorption and desorption, making the total system more complex and costly.

In order to increase the selectivity of solid sorbents to CO_2 , amine substances were chemically bonded on various supports, such as foamed polymers [22], mesoporous molecular sieve MCM-42 [23], and mesoporous silicas [10,24]. The novel solid adsorbents are currently popular worldwide because of their advantages of high selectivity to CO₂, easy regeneration, and low corrosion to experimental equipment. The adsorption capacity is determined by amine substances, whereas the specific surface area of mesoporous materials decides the interface area between the amine material and support. The existence of residual micropores and medium pores allows CO₂ to be transmitted and rapidly adsorbed. Therefore, it is equally important to evaluate the performance of these carriers. Goeppert et al. conducted a series of studies on the adsorption performance of these types of solid amine absorbents with polyethyleneimine (PEI) as the main adsorbent and various mesoporous materials as carriers, such as fumed silica [25,26] and mesocellular silica foam [27], which has important guiding significance to this study.



Fig. 1. Research framework and structure of this paper.

Table 1

Summary of current CO₂ capture techniques.

CO ₂ capture methods	Materials
Membranes[12,16,17]	Polymeric;
	Inorganic;
	Zeolite;
	Silica
Cryogenics	Cryogenic [13]
Chemical absorption [14]	Monoethanolamine
	Diethanolamine
Physical adsorption	Aqueous adsorbent [18]: Alcohol, polyethylene
	glycol, other oxidizing compounds, Ionic liquids
	Solid adsorbent (amine/polyamine/
	polyethyleneimine physically bonded): activated
	carbon [7,19], silica gel [8,9], alumina, iron oxide
	framework [20], zeolite [21]
	Solid adsorbent (amine/polyamine/
	polyethyleneimine chemically bonded): foamed
	polymers [22], mesoporous molecular sieve
	MCM-42 [23], mesoporous silicas [10,24]

2.2. CO₂ capture systems

2.2.1. Four-bed molecular sieve

To the best of our knowledge, the four-bed molecular sieve (4BMS) (see Fig. 2) is currently the most mature technology for CO_2 adsorption and desorption, with a solid-regenerable molecular sieve commonly used as its adsorbent [28]. However, the molecular sieve must be dehydrated before adsorption because of its low selectivity to CO_2 , and water vapor (H₂O) in air will compete with CO_2 for adsorption. Based on this concept, the 4BMS system consists of two sets of dehydrating beds and adsorbent beds working alternately. In addition, the adsorbent bed is heated at a high temperature and vacuum to desorption and regeneration, and the CO_2 released from desorption is discharged to the outdoor directly. The advantages of the 4BMS system are independent operation and stable and odorless material, which does not require replacement, whereas its disadvantages are also obvious, such as complex system, large size, taxing to operate, and high energy cost.



Fig. 2. Schematic of 4BMS system.

2.2.2. Two-bed molecular sieve

A hydrophobic zeolite molecular sieve is applied in the two-bed molecular sieve (2BMS), eliminating the air-drying process used in 4BMS; thus, continuous adsorption of CO₂ can be realized only by two adsorbent beds working alternately (Fig. 3). According to the same desorption-based method, 2BMS only accounts for half of 4BMS in volume and weight, and it is more energy efficient and simple in operating control. The key point of 2BMS, therefore, lies in the research and application of hydrophobic materials.

2.3. Ultra-low fresh air HVAC system

The so-called ultra-low fresh air HVAC system combines the conventional air-conditioning system with a CTU, processing indoor CO_2 and other contaminants to satisfy the required indoor air quality instead of introducing fresh air. Currently, studies on ultra-low fresh air HVAC systems are primarily focused on space-craft [29,30] and submarines [31,32], where good internal air quality is highly required and outdoor air cannot be introduced. In these confined spaces, lithium hydroxide (LiOH) modules are commonly used to handle CO_2 and activated carbon to remove odors and other contaminants, maintaining good air quality in the absence of outdoor air.

Although existing studies can provide guidance for the design of CTU in this study, the design is particularly based on the entire set of system so that the air treatment unit is installed with the HVAC system as a whole in a special environment. However, it is difficult to integrate these air treatment units with existing airconditioning systems or incorporate the treatment unit with the conventional design because of the high cost of labor and material.





Fig. 3. Schematic of 2BMS system.

Thus, an independent CTU is proposed and investigated in this study. The CTU can be added to an existing system such as radiant ceilings and fan coil systems, avoiding the cost of retrofitting the entire existing HVAC system.

3. Independent CTU design

The design of an independent CTU should follow these rules:

- The adsorbent has a high adsorption capacity for low concentrations of CO₂ (1000–2000 ppm) in air under relatively common conditions;
- The adsorbent should be regenerable to increase replacement cycle;
- The loading process of the absorbent should be easy, and it should be considered in the structure design of the independent CTU;
- 4) The adsorbent should have a good adsorption capacity after many adsorption/desorption cycles without noticeable degradation, ensuring the continuous operation of the CTU;
- 5) The unit should be able to switch easily between adsorption and desorption processes.

3.1. Adsorption material selection

We reviewed and analyzed existing studies on different amine materials and their effectiveness (Table 2). The adsorption/desorption capacity of materials, loading methods (grafting, in-situ polymerization, and impregnation), loading conditions (type, molecular weight, loading capacity, and mesoporous structure), and environment requirements (temperature, concentration, wind speed, and humidity) were summarized and compared. At the end, HP2MGL-PEI (600)-50, a type of PEI-based mesoporous carbon, was selected as the final CO₂ adsorbent due to its comparatively high adsorption capacity per unit volume and easily achievable experimental conditions. The experimental studies show that the equilibrium adsorption amount of HP2MGL-PEI (600)-50 for 400 ppm CO₂ was approximately 1.95 mmol/g.

3.2. Adsorbent properties

3.2.1. Effect of H₂O on adsorption

Studies show that the molecular sieve and zeolite can simultaneously adsorb H_2O and CO_2 , meaning that H_2O and CO_2 may compete with each other and result in reduced adsorption capacity toward CO_2 [40,41]. The adsorption of solid amine adsorbent consists of both physical and chemical processes. In the physical

Table 2

Characteristics of different materials.

Туре	Material	Pressure	C _{CO2} (%)	T_{ad} (°C)	T_{de} (°C)	Q _{ad} (L/min)	Q _{de} (L/min)	M (mmol/g)
Activated carbon	AC1-AC6 [33]	100 kPa	/	0	0-38	1.8	/	2-3.4
	palm kernel shell AC [34]	1 bar	99	25	/	1	1	2.13
	granular coconut shell AC [35]	1 atm	10	35	110	0.09	0.09	0.62
Solid amine sorbent	FS-PEI-50 [26,27]	1 atm	0.04	25	85	0.335	0.335	1.68
	MCF-PEI25k-50 [28]	1 atm	95	25	85	0.06	0.06	1.78
	FS-PEI [36]	1 atm	10	50	110	1	1	2.27
	MC-1.5-PEI (600)-65% [37]	100 kPa	5	75	110	0.05	0.05	4.26
	MC-1.5-PEI (60)-65%-Span-5 [37]	100 kPa	5	75	110	0.05	0.05	4.69
	MC-1.5-PEI (60) [37]	100 kPa	5	30	110	0.05	0.05	3.82
	MCS-1.5-PEI (60)-Span-5 [37]	1 atm	0.5	25	110	0.05	0.05	2.70
	HP2MGL-PEI-50 [38]	1 atm	15	25	100	0.05	0.1	3.41
	HP2MGL-PEI-50 [38]	1 atm	0.5	25	100	0.05	0.1	2.13
	HP2MGL-PEI-50 [38]	1 atm	0.04	25	100	0.05	0.1	1.95
Zeolite	Zeolite 13X [39]	>2bar	0.1	5	25	1	0.4	0.05
Molecular sieve	molecular sieve [40]	133 kPa	15	30	100-131	1	1	0.88

Note: C_{CO2} : Initial CO_2 concentration; T_{ad} : Adsorption temperature; T_{de} : Desorption temperature; Q_{ad} : Air flow rate for adsorption; Q_{de} : Air flow rate for desorption; M: Adsorbent capacity; AC: Activated carbon; FS: Fumed Silica; PEI: Polyetherimide; MCF: Mesocellular foams; MC: Mesoporous carbon; HP2MGL: Macroporous adsorption resin.

process, it is important to consider the adverse effect of moisture on the adsorption performance.

Within a certain relative humidity (RH) range (10–40%), the water film on the outer surface of amine adsorbent and the inner surface of the pore cause more amine groups participating in the reaction. Thus, the water film improves the utilization rate of amine and increases the CO_2 adsorption capacity per mass unit of adsorbent. However, when RH reaches 60%, the water film on the inner surface of the adsorbent particle is excessively thick due to the high proportion of water in the gas flow. This increases the diffusion resistance of CO_2 in the water film and thus reduces the CO_2 adsorption capacity per mass unit of adsorbent. Therefore, the influence of H_2O on the adsorbent can be neglected as long as the indoor air humidity can be controlled within a certain value.

3.2.2. Effect of O_2 on adsorption

The atmosphere contains approximately 78% N₂ and 21% O₂, both of which may be absorbed by adsorbents and therefore hinder the adsorption of CO₂. In the case of 5000 ppm CO₂ and 20.69% O₂, for example, the adsorption capacity of HP2MGL-PEI-50 is slightly reduced, possibly because part of the amine groups in the adsorbent molecule is oxidized by the physically adsorbed O₂, leaving the partial amine groups inactive and unable to absorb CO₂. However, the presence of O₂ in air is unavoidable in practical applications. Because HP2MGL-PEI-50 has a good CO₂ selectivity, its adsorption of O₂ can be ignored, and further study, if necessary, can also be implemented to explore the effect of O₂ on the CO₂ adsorption performance of solid amine adsorbents.

3.2.3. Stability of adsorbent

Stability is another important aspect in selecting solid amine adsorbents. Stability refers to the change in CO_2 adsorption capacity after numbers of adsorption/desorption cycles. Because of the existence of amine groups, solid amine adsorbents are confronted with some problems, mainly the degradation of amine substances over time. Studies pointed out that the degradation of amines substantially involves three different mechanisms: thermal degradation (such as evaporation and decomposition), CO_2 -induced degradation, and oxidative degradation.

For the thermal degradation, Heydari-Gorji and Sayari [42] carried out a study on SBA-15PL-PEI, revealing that PEI-impregnated materials had good thermal stability at moderate temperatures and were not prone to thermal degradation. For instance, PEI with a molecular weight of 600 lost only 1 wt% and 4 wt% at 105°C and 120°C, respectively. Based on this result, the thermal degradation of PEI can be ignored as the desorption temperature was $95^\circ\!\!\mathbb{C}$ in this study.

For the CO₂-induced degradation, Sayari et al. [43] reported that all amine materials, except for secondary monoamines, were significantly deactivated in the presence of dry CO₂ even under mild conditions due to the formation of urea linkages at the expense of amine groups. On the other hand, the existence of H₂O can prevent the reaction between CO₂ and amine groups and the production of urea. Therefore, CO₂-induced degradation can also be neglected because the mixed gas to be processed is moist air in practice, especially in this study.

For the oxidative degradation, studies indicated that the desorption ratio of HP2MGL-PEI (600)-50 can be as high as 96% at 95°C, if N₂ is used as the sweeping gas, meaning that the material can be almost completely regenerated. Moreover, the adsorption amount remained almost the same after 10 adsorption/desorption cycles, showing an excellent cyclic performance in practical applications. In this study, therefore, N₂ was used as the sweeping gas to prevent amine groups from being oxidized in the desorption process.

3.3. System design

Based on the review of CO₂ adsorption and desorption technologies in Section 2, and the performance of HP2MGL-PEI-50 in Section 3.1 and 3.2, an independent CTU was designed and built by using this material. Considering that solid amine adsorbents have a high tolerance for H₂O, it is not necessary to dehydrate or pretreat air with the usage of 4BMS. Conceptually, this solid amine adsorbent is similar to a hydrophobic molecular sieve; therefore, the treatment unit was designed similar to the structure of 2BMS. Nonetheless, the 2BMS system is still a little more structurally complex because it has two adsorbent beds for adsorption/desorption cycle. As a result, only one adsorbent bed was taken, and the adsorption and desorption processes were implemented alternately in the same bed. The unit can be defined as a one-bed molecular sieve (1BMS), which largely simplifies the structure design, reduces processing difficulty and raises economic efficiency (Fig. 4(a)). In addition, the CTU system also extends the application of CO₂ removal technology from large scale (aircrafts, submarines, power plant, etc.) to small scale (normal room conditions) to improve energy efficiency. After determining the system structure of CTU, relevant parameters were designed and calculated, and appropriate equipment was selected for system construction, which is shown in Fig. 4(b).



Fig. 4. Independent CO₂ treatment unit.

4. Experimental results and discussion

4.1. Experimental setup

The experimental platform is built on the "Building Energy Efficiency Laboratory" in Shanghai, China. The whole test platform is composed of two identical rooms and an environment control chamber (Fig. 5(a)). The chamber and the rooms are equipped with two independent air conditioning systems to control the air temperature inside and outside the rooms. The experiment of this study was carried out in Room 1.

The experimental parameters include indoor environment parameters, adsorption and desorption process parameters. The schematic of the system and the location of main sensors are shown in Fig. 5(b). Comprehensive information of all these sensors is presented in Table 3.

The indoor environment parameters consist of indoor air temperature and RH. The sensors were located at a height of 1 m in the center of the room, more than 1 m away from experimenters, CTU, and other experimental objects, to eliminate unnecessary interference to testing data. The temperature and RH are not identical during the test but within reasonable range (20-25°C for temperature and RH < 60%) based on Section 3.2. It is because we aim to verify whether the material is suitable to adsorb CO₂ within the range of operation, instead of testing the material's chemical properties itself. The parameters of the adsorption process include indoor CO₂ concentration, outlet CO₂ concentration of adsorbent, and outlet air velocity of CTU. On the other hand, the parameters of the desorption process consist of the inlet and outlet CO₂ concentration of CTU, temperature setpoint of heater, inlet and outlet air temperature of CTU, and flux of N₂. In this experiment, we selected GSS-COZIR CO₂ sensor with a range of 0–5000 ppm, which was calibrated by standardized TELAiRE CO₂ sensor. The concentration data measured by the CO₂ sensor are updated every 10 s. The temperature of the heater is almost the same as the temperature of the processing gas after it passes through the heater, i.e., the desorption temperature.

After the independent CTU was built, the performance of the unit was tested through experiments. The experiments and design optimization consist of three parts: adsorption and desorption capacity measurements under various operating conditions, cyclic adsorption–desorption performance measurements, and parameter optimization of the CTU.

4.2. Adsorption and desorption capacity measurements of adsorbent

The test parameters of the adsorption and desorption capacity of HP2MGL-PEI (600)-50 under various operating conditions are presented in Table 4. Fig. 6 illustrates the effect of air velocity on the adsorption capacity before (V_1, V_2, V_3) and after (V_4) desorption, where the ordinate represents the effective adsorption coefficient, i.e., the ratio of the outlet CO₂ concentration in the outlet valve of the CTU of the adsorbent to that of the inlet valve of the CTU (see Fig. 4(a)). The effective adsorption coefficient reflects the adsorption capacity of the material: the smaller, the better. Solid lines in Fig. 6 show that the adsorption capacity was the highest at the minimum air velocity of 0.85 m/s. This is because the adsorbent has more time to thoroughly contact CO₂ at lower velocity when air can flow evenly through the material. However, CO₂ cannot be fully caught when air flows too fast. The effective adsorption coefficient under V_2 is higher than that under V_3 in this case since the



Fig. 5. Test platform.

Table 3

List of sensors.

Senso	r Parameter	Туре	Range	Precision
S-Cin S-Cou	Inlet CO ₂ concentration of CTU t Outlet CO ₂ concentration of CTU	GSS-COZIR CO ₂ sensor	0–5000 ppm	±50 ppm ± 3%
S-TH	Indoor air temperature and relative humidity	WSZY-1 temperature and relative humidity recorder	-40 to 100 °C	±0.5 °C
S-Tset	Temperature Setpoint of heater	Type-K thermocouple thermometer	0-400 °C	±0.5 °C
S-T1	Inlet air temperature of adsorbent	HT-L13 four-channel thermocouple thermometer	0-500 °C	±0.5 °C
S-T2	Outlet air temperature of adsorbent			
S-Vin	Inlet air velocity of CTU	SMART SENSOR AR866	0-30 m/s	±1% ±0.1
S-Vou	t Outlet air velocity of CTU			
S-M-N	I ₂ Flux of N ₂ during desorption process	Float flowmeter	3–30 L/min	Level 4

Table 4

Measurements of adsorbent capacity.

No.	Control variable	Load (mL)	Temperature (°C)	RH (%)	Velocity of air (m/s)	Flux of air (m ³ /h)
1	Air velocity	20	21.2	38.70%	0.85	11.77
2			22.1	23.70%	1.80	24.93
3			21.6	27.30%	2.37	32.82
4	Desorption	20	22.1	23.70%	0.91	12.46



Fig. 6. Adsorption and desorption capacity measurements.

adsorbent was kept contact with the air before the test, and the adsorption was a failure.

The dashed line in Fig. 6 shows adsorption performance after desorption. The desorption temperature was set to 95° C with the N₂ flux of 10 L/min and air velocity of 2.3 m/s. It can be observed that the adsorption capacity slightly decreased after desorption. In fact, a portion of the material got saturated when it was exposed to the atmosphere during the process of transferring. Overall, however, the adsorbent performance was still satisfactory after desorption with lower air velocity (0.85 m/s).

4.3. Cyclic adsorption-desorption measurements of CTU

The performance measurement of the entire CTU system was conducted after evaluating the adsorption and desorption capacity of the adsorbent. Since the CTU was placed in the environment for a long time and the adsorbent was saturated with CO₂, the desorption process preceded the adsorption to ensure that both processes were successively completed without exposing to ambient air during transferring, as shown in Fig. 7.

Fig. 8 plots the desorption and adsorption processes of the CTU. The curve between 1000 s and 3000 s can be used to study desorption performance of the adsorbent and that between 4000 s and 8000 s can be used for the analysis of the adsorption performance. At the beginning, a continuous supply of N_2 was required to empty

the CO₂ remaining in the CTU, with the inlet and outlet air valves closed and desorption outlet open, and the fan being adjusted to an appropriate velocity. At 1000 s, the concentration of CO₂ was approximately 0 ppm when the heater was open for desorption. During the desorption process, the CO₂ concentration at the CTU outlet increased to the maximum but soon dropped to 0 ppm again under the scavenging of N₂ at 3000 s, indicating that the desorption process is completed. The CO₂ concentration in the CTU was kept at approximately 0 ppm until the temperature was reduced to approximately 30°C, ensuring the adsorption process to be completed at room temperature (20 °C-30 °C). Meanwhile, N₂ as the sweeping gas should be transported into the unit until the adsorption began. At 5000 s, when the temperature was reduced to 30°C, the adsorption process started, and the inlet and outlet air valves were open, and the desorption valve was closed. At the end, the CO₂ concentration was approximately stable at the outlet of the CTU, indicating the completion of adsorption.

It is worth noting that because of the characteristics of the absorbent material (HP2MGL-PEI (600)-50), the detachment of amine only begins to happen when the temperature is high (>60 °C) [37]. In addition, the exhaust after desorption at high temperature will be discharged outside the room. Therefore, the harm to human caused by amine could be negligible in this experiment. Future studies could focus on the treatment of the exhaust to reduce the harm brought to the outdoor environment.

4.4. Parameter optimization of CTU

We tested the adsorption–desorption performance of the CTU under different conditions to supply a theoretical basis for the design optimization of the independent system.

4.4.1. Operation variables of adsorption process

The operation variables of the adsorption process include the fan speed, adsorption temperature, and adsorbent amount (Table 5). Here, we define two parameters to assist analysis: the adsorption penetration time and the adsorption saturation time. The adsorption penetration to that of the inlet is 5%, which is the duration of maximum use of adsorption capacity. The adsorption saturation time is the time when the router CO₂ concentration accounts for 95% of that in the inlet, revealing the overall adsorption saturation time, the earlier the adsorbent reaches the saturation state



Fig. 7. Internal structure (a) and desorption test (b) of CTU.



Fig. 8. Adsorption-desorption profile of CTU.

and vice versa. However, the adsorption saturation time is not the only standard to evaluate the adsorption capacity of the adsorbent. The effective adsorption coefficient should also be taken into consideration. Generally, a smaller effective adsorption coefficient indicates a longer adsorption saturation time, i.e., the two assessment indices are negatively correlated.

The results of experiments on the variable control of the adsorption process are shown in Fig. 9. Fig. 9(a) demonstrates the adsorption capacity under different air velocities. As can be seen, when the air velocity was at 0.95 m/s, the effective adsorption coefficient was smallest. In addition, the adsorption saturation time under the maximum air velocity was considerably less than the corresponding time under the minimum while the adsorption penetration time was almost all the same. And the differences among three air velocities are consistent with earlier findings, suggesting that the adsorbent has better performance with lower air velocity.

Fig. 9(b) shows the adsorption capacity of the adsorbent at various temperatures. Overall, the adsorption saturation time was all approximately 3600 s at different temperatures. However, the effective adsorption coefficient was noticeably lower at 30°C than the others. This might be depending on the characteristics of the adsorbent that it has relatively high adsorption ability at around 30°C, enabling it to stand a longer adsorption time period.

Compared to the fact that the adsorbent amount in the first five scenarios was 50 mL, as shown in Fig. 9(a) and (b), and the optimal adsorption duration lasted for no more than 1.5 min, the adsorbent volume was increased to 160 mL for the last three scenarios while keeping the optimal adsorption temperature constant (30° C).

Fig. 9(c) shows the adsorption performance of adsorbent at different adsorbent volumes and air velocities. It can be observed that the adsorption penetration time increased and the adsorption effective coefficient decreased with the increased adsorbent volume. It can be concluded that the increment in adsorbent volume had a positive effect on the adsorption performance of the CTU. Results also indicate that the adsorption penetration time and adsorption saturation time were both the longest at a minimum inlet air velocity of 0.95 m/s. Additionally, the effective adsorption coefficient at the minimum air velocity was obviously lower than that of the other two velocities. These results agree with those in Fig. 9(a), showing that the adsorption capacity of the adsorbent was at optimum with the lower air velocity.

4.4.2. Operation variables of desorption process

The operation variables of the desorption process include the flux of N₂, fan speed, and desorption temperature, as presented in Table 6. Fig. 10(a) illustrates the effects of these operational variables in the desorption process. Desorption coefficient is the ratio of the outlet CO_2 concentration to the indoor CO_2 concentration, representing the amount of CO_2 desorption. Namely, the higher the desorption coefficient, the larger the amount of CO_2 discharged per unit of time. It can be observed from the three middle curves in Fig. 10(a) that different air velocities only had a slight impact on

Table 5			
Control	of adsorption	process	variables

No.	Control variable	Volume (mL)	Indoor temperature (°C)	Indoor RH (%)	Adsorption temperature (°C)	Inlet air velocity (m/s)	Outlet air velocity (m/s)	Adsorption penetration time (s)	Adsorption saturation time (s)
1	Air velocity	50	20.4	51.5	30	0.95	0.095	100	3700
2			20.0	52.1	30	1.35	0.150	100	3200
3			23.2	47.2	30	2.10	0.450	100	2400
4	Adsorption	50	23.2	37.4	25	0.95	0.095	100	3400
5	temperature		23.6	34.2	40	0.95	0.095	100	3450
6	Adsorbent	160	21.4	33.2	30	0.95	0.095	170	9100
7	volume		24.7	31.4	30	1.35	0.150	150	5900
8			23.6	30.4	30	2.10	0.450	150	5400



(a) Air velocity as control variable

(b) Adsorption temperature as control variable



(c) Adsorbent volume as control variable

Fig. 9. Operation variables of adsorption process.

Table 6Control of desorption process variables.

No.	Controlled variable	Adsorbent volume (ml)	Flux of N ₂ (L/min)	Indoor temperature (°C)	Indoor RH (%)	Desorption temperature (°C)	Inlet air velocity (m/s)	Outlet air velocity (m/s)	Desorption time (s)
1	Air velocity	50	9-12	20.0	52.1	95	0.95	0.095	650
2				21.5	39.4	95	1.35	0.15	650
3				22.2	47.5	95	2.10	0.45	650
4	Desorption	50		23.8	36.6	75	0.95	0.095	630
5	temperature			24.1	32.6	50	0.95	0.095	550
6	Adsorbent	160		20.6	52.3	95	0.95	0.095	650
7	volume			21.6	30.8	95	1.35	0.15	670
8				22.8	50.6	95	2.10	0.45	660

the desorption rate and nearly made no difference on the total desorption amount of CO_2 while the other parameters were kept constant. Furthermore, there were also little differences among different velocities on the desorption rate as well as on the overall desorption amount, as shown in the three top curves in Fig. 10(a). However, the increase in adsorbent load increases the total adsorption and desorption amounts of CO_2 . The three bottom curves describe the desorption performance under different desorption temperatures. Results show that the desorption coefficients for both 75 °C and 50 °C were significantly smaller than that for 95 °C, indicating that the adsorbent was not fully regenerated when the temperature was below 95 °C.

Based on the above analysis, we can draw the following conclusions:

- 1) Air velocity had only a slight influence on the desorption rate, while the overall desorption amount of CO_2 was almost the same under different air velocities. However, the desorption temperature had a significant effect on the desorption amount of CO_2 , which determines whether desorption is entirely completed.
- 2) Incomplete desorption would inevitably reduce the adsorption capacity after desorption. As shown in Fig. 10(b), the adsorption saturation time after desorption with the highest



(b) Adsorption with different desorption temperatures (c) Adsorption performance before and after desorption under the same conditions



temperature was obviously longer than that with lower desorption temperatures, indicating that the higher the desorption temperature, the more completely desorption. On the other hand, the adsorption capacity was almost the same as normal after desorption at 95 °C, as shown in Fig. 10(c). This confirmed that the complete desorption was achieved at 95 °C.

Overall, the experimental results show that the solid amine absorbent could not only has good adsorption capacity in processing the power plant flue gas (high temperature, high pressure, high CO_2 concentration), it could also be used under normal atmospheric pressure, temperature, RH, and low CO_2 concentration in reality -- the CTU shows good cyclic adsorption–desorption capacity under certain conditions which are easily to implement. The indoor CO_2 concentration could be reduced to a favorable level by using CTU. In addition, the adsorption–desorption performance of the CTU was tested under different conditions, which can be used as the theoretical basis for the design optimization of the independent CTU system. In this paper, only two cases of adsorbent amount were considered. Results show that when the air velocity is within a proper range (i.e., overcome the resistance), the adsorption penetration time increased and the adsorption effective coefficient decreased, namely, the adsorption performance increases with the increase of the material amount. In fact, there should be an optimal adsorbent amount under every operational condition (certain air velocity, temperature, equipment size, etc.). In this paper, however, we mainly focus on one CTU unit, and experiments were implemented to verify the adsorption and desorption performance of this particular material as well as the feasibility of the designed CTU unit in real buildings, instead of concluding the optimal performance among different units. As long as the material amount is less than this maximum value, the adsorption performance will increase within that range.

5. Modeling analysis

Based on the experimental study in Section 4, the unit was simulated to determine the optimal operation conditions. The simulation involved a room where the indoor CO_2 concentration was changed with the application of the CTU. Moreover, an ultra-low fresh air HVAC system simulation model was built by combining the CTU and the existing air-conditioning system. Energy Plus was used to simulate the energy consumption in order to evaluate its energy savings.

5.1. Indoor CO₂ concentration change with CTU

5.1.1. Simulation conditions

The experimental space was a room with dimensions of 4.6 \times 3. 2 \times 2.7 m (length \times width \times height). It was assumed that humans were the only source of CO₂ in the confined room with a natural air change rate of 0.17 h⁻¹ and an outdoor CO₂ concentration of 370 ppm. The calculation equation of human CO₂ release rate is as follows [44]:

$$V_{\rm CO_2} = \frac{165.6A_{\rm D} \cdot M}{0.23RQ + 0.77} \tag{1}$$

$$Q = V_{\rm CO_2} \cdot RQ \cdot n \tag{2}$$

where V_{CO_2} is the oxygen consumption rate, RQ is the respiration coefficient, A_D is the DuBois surface (m²), M is the metabolic rate per surface depending on the state of human activity, Q is the CO₂ release rate, and n is the number of people. According to ASTM D 6245–98 [45], RQ is 0.83 for a person of medium figure in a light activity or sedentary state, and the human CO₂ release rate is equal to the oxygen consumption rate times the respiration coefficient. A_D is 1.8 m² for an adult with a height of 1.78 m and a weight of 65 kg according to Exposure Factors Handbook [46].

The following assumptions were made in the simulation. The CO_2 treatment system was considered as airtight with no air leakage. Therefore, the air volume at the outlet was equal to that at the inlet. We also assumed that the HVAC air change rate was one air change per hour; thus, the circulation air volume was approximately 40 m³/h. We set the desorption temperature at 95 °C, the same as the optimal desorption temperature in the experimental result. The adsorption performance remained almost the same after 10 adsorption/desorption cycles in Section 3.2.3 when we discuss the stability of the adsorbent. Moreover, experimental results showed that there was no performance degradation during our testing period. Therefore, we assumed that this solid amine material could be regenerated as many times as needed in the simulation.

5.1.2. Room CO₂ concentration

We assumed a homogeneous CO_2 in the room space. According to the mass conservation equation, when humans are considered as the single source of CO_2 in a room, the variation in indoor CO_2 concentration is

$$V \cdot \frac{dC_i}{dt} = V \cdot \mu \cdot (C_o - C_i) + n \cdot Q$$
(3)

where C_i and C_o are the indoor and outdoor concentration of CO_2 (ppm), μ is the air exchange rate (h⁻¹), V is the volume of room (m³), Q is the CO₂ release rate (mL·min⁻¹·person⁻¹), and n is the number of persons indoor.

Suppose that the room is empty except for the period from 8:00 to 18:00 in a day, and the indoor CO_2 concentration is 370 ppm at the initial moment, which is the same as the outdoor concentration. Based on experimental results, the optimal adsorption conditions were selected to simulate and calculate the variation in CO_2 concentration in the room. According to the CO_2 concentration profile, the independent CTU started working at 10:00. The mass balance equation of the indoor CO_2 concentration is adjusted as follows with the operation of the CTU:

$$V \cdot \frac{dC_i}{dt} = V \cdot \mu \cdot (C_o - C_i) + n \cdot Q - q \cdot \Delta C$$
(4)

where $q \cdot \Delta C$ is the variable quantity of indoor CO₂ concentration caused by CTU, q is the circulation air volume (m³/h), and ΔC is

the amount of CO₂ absorbed by the CTU for a certain time, which indicates the adsorption capacity of the system.

The variations in indoor CO_2 concentration with the CTU were calculated by simulation and compared with that without the unit (Fig. 11(a)). Fig. 11(a) shows that the indoor CO_2 concentration decreased significantly after operating the CTU. After a few minutes, the indoor CO_2 concentration was as low as 0 ppm and remained below 500 ppm in the first 1.5 h. However, when the adsorbent started to saturate gradually, the amount of CO_2 absorbed by the unit decreased. Notice that the adsorption rate of the system was very low during the last period when the adsorbent was almost saturated. The final CO_2 concentration exceeded 1000 ppm.

Therefore, it was necessary to develop appropriate control strategies to achieve a continuous adsorption–desorption cycle of operation to ensure an indoor CO₂ concentration consistently below the upper limit of 1000 ppm.

The adsorption property of the solid amine adsorbent (HP2MGL-PEI (600)-50) indicates that its adsorption period is about 2 h [37]. Accordingly, two operating control strategies were designed, as presented in Table 7. Strategy I takes 1 h as the time interval between adsorption and desorption for the adsorption-desorption cycle, whereas Strategy II takes 1.5 h for the adsorption process and 1 h for the desorption process.

After determining the two control strategies, the variation in indoor CO_2 concentration was simulated in one day. Then, the results of indoor CO_2 concentration variation with the air treatment unit were compared.

Fig. 11(b) shows the variation in indoor CO_2 concentration with the implementation of the two control strategies. The indoor CO_2 can be maintained below the standard value of 1000 ppm under Strategy I. Overall, Strategy II also met the requirements except for the peak value exceeding 1000 ppm in some short periods. The time not satisfied accounted for approximately 6.25% of the total time, with a variance of not more than 100 ppm above 1000 ppm. From the perspective of energy consumption, Strategy I bears higher than Strategy II with half more adsorption–desorption cycle. However, Strategy II cannot fully satisfy the CO_2 standard requirement. Both control methods are simple strategies. Ideally, a feedback control loop is necessary to alternate automatically between adsorption and desorption according the indoor CO_2 concentration and hours of operations. From

Fig. 11, we could see that the independent CTU effectively handles indoor CO_2 concentration with the continuously cyclic adsorption and desorption processes for one day, which indicates the practicability and validity of this proposed CTU in real building environment.

5.2. Modeling of ultra-low fresh air HVAC system

The modeling of indoor CO_2 concentration in Section 5.1 describes how this air treatment unit handles indoor CO_2 . On this basis, an ultra-low fresh air HVAC system model was created by combining the CTU with the existing air-conditioning system. Therefore, we can use this model to simulate the energy consumption and analyze the energy efficiency.

The location of the simulated building is in Shanghai, China. Shanghai has a subtropical climate with four distinct seasons every year, including spring (March to May with an average temperature 14.5–16.2 °C), summer (June to August with an average temperature 27.0–28.5 °C), fall (September to November with an average temperature 19.3–20.8 °C), and winter (December to February with an average temperature 4.7–6.0 °C) [47]. A small office building model with a relatively simple structure was built in Energy Plus to simulate the energy consumption. This building was a one-story building, which was divided into four exterior and one



Fig. 11. CO₂ concentration variation.

Table 7Two operating control strategies.

Strategy I		Strategy II	
8:00-10:00	OFF	8:00-10:00	OFF
10:00-11:00	AD	10:00-11:30	AD
11:00-12:00	DE	11:30-12:30	DE
12:00-13:00	AD	12:30-14:00	AD
13:00-14:00	DE	14:00-15:00	DE
14:00-15:00	AD	15:00-16:30	AD
15:00-16:00	DE	16:30-17:30	DE
16:00-17:00	AD	17:30-18:00	AD
17:00-18:00	DE	18:00~	OFF after DE
18:00~	OFF		

Note: AD and DE are abbreviations for adsorption and desorption, respectively.

interior conditioned zone. For HVAC system, four-pipe fan coil system with dedicated outdoor air system was used, served by hot water for heating and chilled water for cooling. Central plant was single hot water boiler and electric compression chiller with cooled condenser. Zone temperature control was the dual setpoint (heating and cooling) with dead band.

5.2.1. Fresh air volume

Office hours were from 7:00 to 19:00 on weekdays, and schedules for personnel, lighting, and equipment were slightly adjusted based on the schedule provided by Energy Plus.

In the conventional design specifications of the HVAC system, the fresh air volume is determined by three factors: infiltration air volume required to maintain the indoor positive pressure, minimum fresh air volume satisfying the hygienic requirements, and 10% of the total air volume of the system. The maximum value is used as the design fresh air volume of the HVAC system. In practice, however, the fresh air volume is determined according to the specification for the hygienic requirements, which is 0.00944 m³·s⁻¹·person⁻¹ in the benchmark model.

With the application of the CTU, there is no need to bring in fresh air to dilute CO_2 . The other contaminants such as VOCs can be filtered or absorbed by other devices (these devices are not within the scope of this discussion). The fresh air volume, therefore, only needs to balance the infiltration volume required to maintain the indoor positive pressure, preventing outdoor pollutants from infiltrating into the room. Generally, the indoor positive pressure is approximately 5–10 Pa, because an excessive positive pressure is neither necessary nor beneficial to reduce the economy

of system operation. Therefore, an indoor positive pressure of 5 Pa was selected as the basis of infiltration air volume in this study.

The infiltration air volume of passive buildings in natural state is close to 0, but it is demanding for civil buildings. Considering the actual situation of construction, we chose a level II tightness (Fig. 12) for design and calculation, which was suitable for the unfixed wooden window with 0.2–0.3 mm wide gap covered with sealing strips. Accordingly, the fresh air volume required for each area was obtained, as listed in Table 8.

5.2.2. Energy-saving analysis

Table 9 presents the results of energy consumption of the building before and after the modification. We can see that the heating and cooling energy consumption have been largely decreased compared with the benchmark model. The annual energy consumed for the regeneration of the CTU and the energy consumption in obtaining adsorption-required N₂ have also been calculated and included in Table 9. Currently, N₂ for industrial use is mainly obtained through air separation technology and the specific power consumption of liquid nitrogen (-196 °C at normal condition) is 0.549 kWh/kg through a standard air separation unit [48]. We used



Fig. 12. Infiltration air volume per m of gap under internal and external pressure differences.

Table 8

Fresh air volume in various areas.

No.	Area (m ²)	Volume (m ³)	Total length of gap (m)	Infiltration air volume rate (m ³ /s)
Space1	99.16	239.25	36.4	0.00506
Space2	42.73	103.31	17.6	0.00244
Space3	99.16	239.25	36.4	0.00506
Space4	42.73	103.31	17.6	0.00244

Table 9

Annual energy consumption statistics and comparison.

Model	Cooling (kWh)	Heating (kWh)	$N_{2} (Nm^{3})$	Annual energy consumption (kWh)				Energy savings	
				Electricity	Gas	CTU	N_2	Total	
Benchmark Ultra-low fresh air	15,764 10,519	3181 694	/ 4.3	53,325 46,647	3181 694	/ 1717	/ 2.8	56,506 49060.8	/ 13.18%

this value and converted it to volume by the density of liquid nitrogen (810 kg/m³) to estimate the energy necessary to obtain N₂. As a result, the total amount of energy savings for the building was approximately 13.18% using the ultra-low fresh air model. Therefore, it can be concluded that the combination of CTU and airconditioning system can reduce the fresh air volume significantly, ultimately reducing the energy consumption of the HVAC system. In addition, more improvement in the air tightness of the building can further reduce the energy consumption by fresh air.

From the energy-saving analysis results, we could conclude that the independent CTU could bring extra energy saving by using adsorption-based method instead of the ventilation-based method to remove CO₂, thus reducing the required amount of outdoor air and fresh air load to save energy in HVAC systems of real buildings.

5.2.3. Economic analysis

The economic feasibility of the ultra-low fresh air HVAC system with implementation of the CTU has also been assessed compared to the benchmark. For both benchmark and ultra-low fresh air HVAC systems, investment costs and energy costs (electricity and natural gas) were calculated. The investment costs were calculated based on the information provided from the manufacturers and suppliers. The energy costs were calculated by using the average electricity price (\$ 0.103/kWh) and natural gas price (\$ 0.46/Nm³) in Shanghai, China.

Based on these estimations, the results of the cost analysis are presented in Table 10. The main cost of the ultra-low fresh air system is related to the solid amine material and N₂, which accounts for approximately 96% of the initial investment cost. Since the solid amine we used in this research is a new material, this cost could be

Table 10

Economical	analysis	of the	ultra-low	fresh	air	HVAC s	vstem.
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	Item	Ultra-low fresh air	Benchmark
Investment costs (\$)	Solid amine	1,535	/
	Fan	46	
	Heater	73	
	Portable smart	10	
	thermostat		
	N ₂	2,500	
	Other materials	28	
	Total initial cost	4,192	
Energy cost (\$)	Electricity	4,981	5,492
	Gas	29	130
	Total energy cost	5,010	5,622
	Energy cost savings	612	1
Static payback time (year)	6.85		-

largely reduced when the material gets industrialized and widely used. The cost for N_2 could also be reduced with more advanced air separation technologies and systems in the future.

The energy cost savings of the ultra-low fresh air HVAC system is about \$ 612 per year, mainly due to the significant heating and cooling energy reduction, as we can see in Table 9. The static payback time is calculated as the initial investment costs divided by the annual energy cost savings, which is approximately 6.85 years.

6. Conclusions

Fresh air load is an important factor in reducing building energy load since a large amount of fresh air is needed to meet the high requirement of indoor air quality and ventilation. After reviewing various CO_2 capture materials and methods, CO_2 capture systems, as well as the current non-fresh air systems in aircrafts and submarines, an innovative independent CO_2 treatment unit (CTU) with the solid amine adsorbent (HP2MGL-PEI (600)-50) was designed and investigated. This CTU uses pollutant purification theory to remove CO_2 instead of the conventional fresh air dilution method, which could largely decrease fresh air load in HVAC systems.

Experimental investigation and robust theoretical simulations were carried out to verify the feasibility and efficiency of the CTU. Overall, the experimental results show that the solid amine absorbent could not only has good adsorption capacity in processing the power plant flue gas, it could also be used under normal atmospheric environment in reality -- the CTU could effectively decrease the CO₂ adsorption coefficient before and after the desorption process under certain conditions. The indoor CO₂ concentration could be reduced to a favorable level by using this CTU. In addition, the adsorption-desorption performance of the CTU was tested under different conditions to achieve optimization, which can be used as the theoretical basis for the design optimization of the independent CTU system. Results show that the adsorbent has better adsorption performance with lower air velocity; however, air velocity had only a slight influence on the desorption performance. The temperature has effects on both adsorption and desorption properties: the optimal adsorption and desorption temperatures are 30 °C and 95 °C, respectively. An increment in adsorbent volume (50-160 mL) could also improve the adsorption performance.

After verifying the practicability and effectiveness of this CTU, the simulation outcomes in Section 5 further shows the actual ability of this unit in reducing indoor CO₂ centration through pure physical and mathematical equations, and HVAC energy savings through robust energy simulation tools. Results indicate that the indoor CO₂ could be kept under 1000 ppm with the continuously cyclic adsorption and desorption processes for one day under proper control strategies. The fresh air load was significantly reduced. The amount of energy savings of the reference building was approximately 13.18% in this paper. The economic analysis show that the static payback time of the ultra-low fresh air HVAC system was approximately 6.85 years. In the future, more studies could be implemented to optimize the material amount to balance the primary cost of CTU and the operation cost with the number of cycles needed to maintain the CO_2 concentration in real buildings.

CRediT authorship contribution statement

Yiyi Chu: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Writing - original draft, Writing - review & editing, Validation. **Peng Xu:** Conceptualization, Formal analysis, Funding acquisition, Supervision, Writing - review & editing, Validation. **Yunfei Jia:** Conceptualization, Formal analysis, Investigation, Methodology, Writing - original draft, Writing review & editing, Validation. **Meishun Lin:** Investigation, Visualization, Project administration, Validation. **Cheng Peng:** Project administration, Resources, Software. **Qiang Dou:** Visualization, Resources, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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