

Experimental Study on the Effects of Humidity, Carbon Dioxide, and Carbon Monoxide on Pressure Swing Adsorption Oxygen Production and Their Removal

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Abstract

Pressure swing adsorption (PSA) oxygen generators are widely used for on-site oxygen supply in plateau tunnels, mines, and other confined engineering environments, where feed air may contain high humidity, carbon dioxide (CO₂), and carbon monoxide (CO). This study experimentally evaluated the effects of these impurities on a two-bed PSA oxygen-generation system and investigated corresponding removal strategies. At 25% relative humidity (RH), product oxygen concentration remained nearly stable during 90 min of operation, whereas at 80% RH it decreased by 15.7 percentage points. Incorporating activated alumina at the bottom of the adsorption beds mitigated moisture effects; with a 1:1 activated alumina-to-zeolite mass ratio, oxygen concentration remained nearly unchanged from 50% to 80% RH. Increasing inlet CO₂ from 0% to 3% decreased oxygen concentration by 2.9 and 8.9 percentage points at product-gas flow rates of 1 and 4 L/min, respectively, while a silica-gel guard layer suppressed this deterioration. Molecular-sieve beds alone did not achieve deep CO removal. Downstream Hopcalite reduced CO below 2 ppm at 1000 ppm inlet CO and 1130 h⁻¹ gas hourly space velocity, demonstrating effective impurity protection for PSA oxygen systems.

1. Introduction

Tunnel construction at high altitude faces many difficulties, not only to overcome the problem of thin air and lack of oxygen (West 2006), coupled with poor ventilation in the tunnel and poor gas circulation in the closed space, resulting in harmful gases that are prone to enrichment. Construction workers undertaking heavy labor under such high-altitude conditions can experience severe hypoxia, and their health cannot be guaranteed. And in serious cases, even life safety is threatened (Guo et al. 2016; Wang et al. 2019; Rosales et al. 2022). At present, the oxygen generation and supply technology based on the principle of pressure swing adsorption (PSA) is commonly used in high altitude region with the advantages of low cost, high safety, small investment, and continuous oxygen supply (West 1995; West 2015).

PSA oxygen generation separates oxygen and nitrogen from air by using the preferential adsorption of nitrogen over oxygen on zeolite molecular sieves under elevated pressure (Sircar 2002; Rege et al. 2000). During the adsorption step, nitrogen is selectively retained in the adsorbent bed, while oxygen-enriched gas is collected as the product. During depressurization and purge, the adsorbed nitrogen is desorbed and the bed is regenerated for the next cycle. Compared with cryogenic air separation (Banaszkiewicz et al. 2014; Wilcox 2012), PSA systems are more compact and suitable for on-site and intermittent oxygen supply. Compared with membrane separation (Murali et al. 2013), PSA can generally provide higher oxygen concentration. Compared with chemical oxygen generation, PSA can operate continuously using air as the feed gas. Therefore, PSA is suitable for plateau tunnels, mines and other confined engineering environments where continuous oxygen supply is required.

However, PSA oxygen generation is sensitive to the quality of the feed gas (Rege et al. 2001). Water vapor is strongly adsorbed by zeolite molecular sieves because of its polarity and strong interaction with

cationic adsorption sites (Epiepang et al. 2016). Once water molecules enter the micropores, they can occupy the active adsorption sites for nitrogen and reduce the effective adsorption capacity of the molecular sieve. CO₂ can also be preferentially adsorbed by zeolites because of its quadrupole moment and strong affinity with polar adsorption sites (Tao et al. 2024). Under insufficient regeneration conditions, CO₂ accumulation may lead to a gradual decrease in oxygen concentration. Therefore, dehydration and CO₂ pre-removal are important for maintaining stable PSA oxygen production (Santos et al. 2008).

High humidity is often a problem during the construction of high-altitude tunnels, as well as CO₂ and CO emissions from the combustion of power machinery in tunnels and high CO₂ naturally seeping out of the tunnels. In addition, the poor ventilation and the large number of construction workers in tunnels lead to poor air quality in tunnels, and the generation of CO mainly originates from the exhaust gas and blast CO emitted by machinery in the construction process (Wu et al. 2022; Wang et al. 2022; Xue et al. 2019). Incomplete combustion of internal combustion engines in highland conditions leads to more serious CO emission problems (Haba and Oancea 2015; Mahmoudi et al. 2017). The generation of CO₂ mainly originates from tailpipe emissions and the natural infiltration of CO₂ in tunnels. CO is a highly hazardous gas that is harmful to the human body in very small quantities, and it is combined with hemoglobin to cause irreversible damage to brain cells (Schmidt et al. 2019; Assadi 2019; Zhao et al. 2019). The presence of CO in tunnels can seriously affect the progress of tunnel construction. Huang et al. (2020) found that the diffusion coefficient of CO is inversely proportional to the altitude, and the higher the altitude, the slower the diffusion of CO in tunnels. Numerous scholars have tested and studied the distribution of CO concentration in tunnels and found that the CO concentration in the working area of construction operations in tunnels after ventilation is generally in the range of 10–30 ppm, with a maximum of more than 50 ppm (Toraño et al. 2011; Sasmito et al. 2013; Li et al. 2016; Y 2024; Zhou et al. 2020).

As the most widely utilized method for on-site oxygen production in plateau areas, PSA uses air as the gas source to produce oxygen. However, the harsh atmosphere inside the tunnel will have different degrees of damage to the oxygen production effect of PSA. However, the current PSA oxygen generation system often has cleaner air, and there is a lack of investigation on oxygen generation and gas purification under high humidity, high CO₂, and CO atmosphere. In PSA oxygen generation, CO₂ should be removed before it reaches the main molecular sieve bed or in the front section of the adsorption bed. This is because CO₂ is strongly adsorbed by zeolite molecular sieves and may occupy part of the adsorption sites that are responsible for N₂ separation. If CO₂ cannot be completely desorbed during the regeneration step, it may gradually reduce the effective adsorption capacity of the bed and cause a decline in oxygen concentration. Therefore, a CO₂ guard layer is required to protect the molecular sieve and maintain stable oxygen production under CO₂-containing feed-air conditions. CO is different from water vapor and CO₂ because it is not only a possible impurity in the feed gas, but also a toxic component that may enter the oxygen-enriched product gas. Although zeolite molecular sieves can

adsorb part of CO during the PSA process, residual CO in the product gas may still cause safety concerns when the oxygen is used for breathing. Therefore, deep CO removal is necessary in PSA oxygen generation systems operating with CO-containing feed air. Catalytic oxidation is a practical method for CO purification because it can convert CO to CO₂ under mild conditions and has been widely studied for low-temperature or room-temperature CO removal (Xie et al. 2009; Oh et al. 2017; Cai et al. 2020; Punde and Tatarchuk 2012; Taylor and Rhodes 2006; Horikoshi et al. 2021). Among various room-temperature CO oxidation catalysts, Hopcalite-type Cu–Mn oxide catalysts have attracted attention because of their low cost and relatively high activity (Brittan et al. 1970; Yoon and Cocke 1988; Fan et al. 2024). However, their catalytic activity is sensitive to humidity. Previous studies have shown that water vapor can cause rapid deactivation of Hopcalite and related CO oxidation catalysts (Brittan et al. 1970; Yoon and Cocke 1988). This deactivation is generally attributed to the competitive adsorption of water molecules on the catalyst surface, which blocks active sites and inhibits CO adsorption and oxidation (Vepřek et al. 1986). Therefore, the placement of the CO catalyst and the humidity level of the gas entering the catalyst layer should be carefully considered in PSA oxygen generation systems.

For CO₂ removal, silica gel is a kind of adsorbent with good pressure reduction and removal at room temperature, which has been widely used in PSA decarbonization (Zhang et al. 1998). For water vapor removal from raw gas, activated alumina is a more suitable adsorbent for dehydration in PSA layered bed (Rege et al. 2001). Still, there is a lack of investigation on the effect of the use of PSA for oxygen production under high humidity conditions.

Although PSA oxygen generation has been widely used for on-site oxygen supply, most existing studies have focused on adsorbent performance, cycle optimization, or oxygen production under relatively clean feed-air conditions. In practical plateau tunnels, mines, and other confined engineering environments, the inlet air may contain high humidity, elevated CO₂, and CO at the same time. These impurities may not only reduce the nitrogen adsorption capacity of the molecular sieve, but also affect the safety of the oxygen-enriched product gas. However, the influence of such contaminated feed air on PSA oxygen production has not been sufficiently quantified, and the protective roles of dehydration, CO₂ removal, and CO catalytic purification in a PSA oxygen generation system remain unclear. Therefore, this study investigated the effects of water vapor, CO₂, and CO on a two-bed PSA oxygen generation system. Activated alumina, silica gel, and Hopcalite catalyst were introduced to reduce the influence of these impurities, and the catalyst position and gas hourly space velocity were further examined for CO removal. The results are expected to provide practical guidance for the design and operation of PSA oxygen generation systems used in high-humidity and contaminated-air environments.

2. Experimental Methods

2.1 Experimental System and Equipment

The experimental setup used to evaluate oxygen production and impurity removal in the PSA system is shown in Fig. 1. The system consisted of three main sections: a feed-gas preparation section, a two-bed PSA oxygen generation section, and a gas analysis section. The oxygen generation section was operated as a two-bed PSA process. The gas source includes two compressors, gas cylinders, mass flow meter, and steam generator, which can generate raw gas with different concentrations of feed gas. The components of the catalytic oxygen generation system include an adsorption bed, a surge tank, a solenoid valve, alumina, a molecular sieve, a CO catalyst, a CO₂ remover, and a mass flow meter. The adsorption bed is mainly used to separate O₂ and N₂, and can be filled with alumina and CO₂ remover to remove water vapor and CO₂. According to the needs of the experiment, the CO catalyst can be loaded in the adsorption bed or in the slow charging canister; the detection end includes an oxygen analyzer and a flue gas analyzer, which are used to detect the concentration of oxygen and the content of impurity gases at the source end, the desorption end, and the product gas end. The parameters of the experimental materials and equipment are shown in Table 1.

Table 1
Parameters Related to Experimental Materials and Equipment

Name of equipment and materials	Manufacturer	Model number	Specification parameter
Compressor a	JiangSu Shink	NZK160P1-30	Rated flow rate 30 L/min
Compressor b	JiangSu Shink	SG10D12-10	Rated flow rate 10 L/min
Gas cylinder	Haipu gas	/	CO concentration 3000 ppm
Mass flowmeter	Assert Instruments (Beijing) Co., Ltd	AST10-DL	Accuracy ≤ 1.5% FS
Adsorption bed	/	/	Length 250 mm, inner diameter 52 mm
Activated alumina	Luoyang Jianlon Micro-Nano New Material Co., Ltd	JLAA-1	Particle size of 0.5 mm- 1 mm
Molecular sieve	Luoyang Jianlon Micro-Nano New Material Co., Ltd	JLOX-101A	Particle size of 0.4 mm- 0.8 mm
CO catalyst	Minsizhuang	AUX-9	Particle size of 1.1 mm
Oxygen analyzer	BEEGAS	BEE-5100	Measuring range 10.00%~99.99%
Flue gas analyzer	Shendawei	SUMMIT708	Range 0–10000 ppm, Accuracy ± 3 ppm

All experiments were conducted at room temperature of 25°C. Compressed air was used as the main feed gas for the PSA system. CO or CO₂ from the gas cylinder was metered by a mass flow meter and

mixed with air before entering compressor B. The gas streams from compressor A and compressor B were further mixed in the buffer tank and then introduced into the PSA adsorption beds as the feed gas. The two adsorption beds were packed with different layered configurations according to the experimental objective. The packing materials included activated alumina, molecular sieve, silica gel, and Hopcalite catalyst. The product-gas flow rate was adjusted by a mass flow meter, and the oxygen concentration was continuously measured at the product-gas outlet. The flue gas analyzer was used to measure CO and CO₂ concentrations at the feed-gas inlet, desorption-gas outlet, and product-gas outlet. The sampling position was adjusted according to the specific experiment.

2.2 Experimental Design and Operating Conditions

2.2.1 General Operating Conditions

Experiments were designed to evaluate the PSA oxygen generation performance under feed gases containing water vapor, CO₂, or CO. Unless otherwise stated, each adsorption bed was packed with 50 g of activated alumina at the bottom and 260 g of molecular sieve above the alumina layer. For each group of experiments, the feed-gas flow rate was kept constant, while the impurity concentration was varied stepwise. The product-gas flow rate was adjusted to 2.0–3.5 L/min using the mass flow meter at the product-gas outlet. The CO, CO₂, and humidity levels were recorded using the flue gas analyzer and hygrometer at selected sampling positions, including the feed-gas inlet, desorption-gas outlet, and product-gas outlet.

2.2.2 Adsorbent and Catalytic Materials

Different adsorbent and catalytic materials were introduced into the PSA system to remove water vapor, CO₂, and CO from the feed gas or product gas. Activated alumina was used for water vapor removal, fine-pore silica gel was used as the CO₂ guard material, and Hopcalite catalyst was used for CO catalytic oxidation. The Hopcalite catalyst had a particle size of 1.1 mm, a bulk density of 0.7 g/mL, and an applicable operating temperature range of 10–400°C. Since the PSA oxygen generation system was intended for room-temperature operation, the CO purification experiment was also conducted under room-temperature conditions. The influence of humidity on CO catalytic oxidation was evaluated by comparing catalyst performance under dried and humid gas conditions.

Before the experiments, the molecular sieve, activated alumina, silica gel, and Hopcalite catalyst were pretreated to remove adsorbed moisture. After pretreatment, the materials were cooled to room temperature in a sealed container before being packed into the adsorption beds or oxygen storage tank.

2.2.3 Humidity Experiment

In the humidity experiment, the effect of relative humidity on oxygen production was first evaluated using the standard bed configuration of 50 g activated alumina and 260 g molecular sieve. A feed gas with 25% RH was used as the control condition, while feed gases with 50–80% RH were used to simulate

high-humidity environments. The product-gas flow rate was maintained at 2 L/min. The oxygen concentration at the product-gas outlet was recorded as the main indicator of PSA performance.

To evaluate the protective effect of activated alumina, the mass ratios of activated alumina to molecular sieve were adjusted to 1:1, 1:2, 1:3, 1:4, and 1:5. The total mass of activated alumina and molecular sieve in each bed was kept at 310 g. The relative humidity of the feed gas was varied from 50% to 80%, and the change in product-gas oxygen concentration was measured under each condition. The 25% RH condition represented relatively dry inlet air, whereas 50–80% RH was used to represent humid tunnel or underground engineering environments.

2.2.4 CO₂ Experiment

In the CO₂ experiment, the effect of CO₂ on PSA oxygen production and the protective effect of silica gel were evaluated. Silica gel was packed at the bottom of the adsorption bed with masses of 0, 50, and 150 g. The 0 g silica gel condition was used as the control. The CO₂ concentration in the feed gas was varied from 0 to 3%, and the product-gas flow rate was adjusted to 1, 2, 3, and 4 L/min. The oxygen concentration at the product-gas outlet was measured under each condition. The feed CO₂ range of 0–3% was selected to cover normal air, CO₂-enriched confined environments, and extreme or stress-test conditions caused by insufficient ventilation or local CO₂ accumulation.

2.2.5 CO Removal and Catalyst Placement Experiment

In the CO removal experiment, six catalyst configurations were compared to evaluate the effect of catalyst position on CO purification. Case 1 was operated without Hopcalite catalyst and was used as the control condition. In Cases 2–4, 35 g of Hopcalite catalyst was placed in the lower, middle, and upper sections of the adsorption bed, respectively. In Cases 5 and 6, 35 g and 70 g of Hopcalite catalyst were placed in the oxygen storage tank, respectively. For all cases, 50 g of activated alumina was packed at the bottom of the adsorption bed, and the remaining space was filled with molecular sieve unless otherwise specified. The oxygen concentration in the product gas was measured using the oxygen analyzer, and the CO concentration in the product gas was measured using the flue gas analyzer. The feed CO concentration was varied from 0 to 1000 ppm. The upper limit of 1000 ppm was used as a stress-test condition to evaluate the CO purification capacity and safety margin of the catalyst bed.

2.2.6 Space Velocity Experiment

To evaluate the effect of gas hourly space velocity on CO catalytic purification, the Hopcalite catalyst layer was placed in the oxygen storage tank, and the catalyst layer thickness was varied from 0 to 40 mm in 5 mm intervals. In this experiment, each adsorption bed was packed with 50 g of activated alumina at the bottom and 260 g of molecular sieve above the alumina layer. The gas hourly space velocity was calculated as:

$$v = Q/V_{cat}$$

where Q is the product-gas volumetric flow rate under ambient conditions and V_{cat} is the volume of the Hopcalite catalyst bed. Complete CO removal was defined as a product-gas CO concentration below the detection limit of the flue gas analyzer or lower than 2 ppm.

3. Results and Discussion

3.1 Effect of Humidity on PSA Oxygen Production

High humidity is commonly encountered in tunnel construction environments and may adversely affect the long-term performance of PSA oxygen generation systems. Therefore, investigating the influence of humidity on PSA oxygen production is essential for ensuring stable oxygen supply under practical operating conditions. The influence of humidity on the oxygen production performance of the molecular sieve bed was first investigated. Figure 2 presents the variation in product-gas oxygen concentration with operating time under different humidity conditions. The product-gas flow rate was maintained at 2 L/min, and each adsorption bed contained 50 g of activated alumina and 260 g of molecular sieve.

At 25% RH, the oxygen concentration remained relatively stable throughout the experiment. No obvious decline in oxygen concentration was observed with increasing operating time. In contrast, under high-humidity conditions (50–80% RH), the oxygen concentration decreased progressively as operating time increased. After 90 min of operation, the oxygen concentration decreased by 7.1, 10.7, 14.4, and 15.7 percentage points at relative humidities of 50%, 60%, 70%, and 80%, respectively.

The results demonstrate that humidity has a pronounced negative effect on the performance of the PSA oxygen generation system. The deterioration became more severe as the relative humidity increased. At low humidity (25% RH), the molecular sieve maintained stable separation performance. However, under humid conditions, water molecules were preferentially adsorbed by the zeolite surface and occupied adsorption sites that would otherwise be available for nitrogen adsorption. This competitive adsorption reduced the effective nitrogen working capacity of the molecular sieve, thereby weakening the N_2/O_2 separation performance of the PSA bed. These results indicate that moisture control is essential for maintaining stable oxygen production. Appropriate dehydration measures should therefore be incorporated into PSA oxygen generation systems intended for humid tunnel or underground environments.

Similar observations have been reported by Santos et al. (2008), who found that water vapor contamination significantly reduced the adsorption capacity of zeolites used in PSA oxygen production. Rege et al. (2001) also reported that water molecules are preferentially adsorbed in zeolite beds and can occupy active adsorption sites, thereby reducing the separation efficiency of the PSA process.

To mitigate the adverse effect of water vapor on PSA oxygen production, activated alumina was introduced as a dehydration layer at the bottom of the adsorption bed. Activated alumina possesses a

high affinity for water vapor and is widely used as a protective adsorbent for feed-air dehydration in PSA systems (Rege et al. 2001). Figure 3 illustrates the effect of the activated alumina-to-molecular sieve ratio on product-gas oxygen concentration under different humidity conditions.

Under the same humidity condition, increasing the proportion of activated alumina significantly reduced the decline in oxygen concentration. At an activated alumina-to-molecular sieve mass ratio of 1:1, almost no decrease in oxygen concentration was observed as the relative humidity increased from 50% to 80%. In contrast, when the activated alumina content was reduced to a mass ratio of 1:5, oxygen concentration decreased markedly as humidity increased, indicating insufficient dehydration capacity.

Increasing the amount of activated alumina increased the water adsorption capacity of the protective layer and delayed moisture breakthrough into the molecular sieve section. Consequently, fewer water molecules reached the molecular sieve layer, allowing the zeolite to maintain a higher effective nitrogen adsorption capacity during PSA operation. As a result, the decline in oxygen concentration was significantly suppressed under humid operating conditions.

From an engineering perspective, increasing the thickness of the activated alumina layer can effectively improve the humidity tolerance of PSA oxygen generation systems used in tunnels, underground mines, and other humid environments. However, excessive alumina loading also reduces the amount of molecular sieve available for nitrogen adsorption. Therefore, the activated alumina-to-molecular sieve ratio should be optimized by balancing dehydration capacity and oxygen production performance. Similar protective effects of feed-air dehydration have also been reported by Rege et al. (2000, 2001) and Santos et al. (2008), who demonstrated that removing water vapor before the molecular sieve bed effectively prolonged the service life of zeolite adsorbents and improved PSA stability. The present results further quantify the required activated alumina loading under different humidity conditions and provide practical guidance for PSA oxygen generation in humid engineering environments.

3.2 Effect of CO₂ on PSA Oxygen Production

Elevated CO₂ concentrations in tunnel construction environments may adversely affect the performance of PSA oxygen generation systems. Therefore, investigating the influence of CO₂ on PSA oxygen production is essential for ensuring the stable operation of oxygen generation systems. The effect of CO₂ on PSA oxygen production was investigated experimentally. Figure 4 shows the variations in product-gas oxygen concentration and CO₂ concentration under different inlet CO₂ concentrations. As shown in Fig. 4, no measurable CO₂ was detected in the product gas over the investigated concentration range. This indicates that CO₂ was preferentially adsorbed by the zeolite molecular sieve. Part of the adsorbed CO₂ could not be completely desorbed during PSA regeneration and therefore remained on the adsorption sites of the molecular sieve. As the inlet CO₂ concentration increased from 0 to 3%, the product-gas oxygen concentration decreased from 92.4% to 90.2%. This behavior can be attributed to the preferential adsorption of CO₂ by the zeolite. Because CO₂ has a stronger quadrupole moment than N₂ and O₂, it interacts more strongly with the cationic adsorption sites and gradually occupies part of the

available microporous adsorption volume (Santos et al. 2008). Consequently, the effective nitrogen working capacity of the molecular sieve decreased, resulting in a gradual decline in the oxygen concentration of the product gas. The results further suggest that incomplete regeneration of adsorbed CO₂ may gradually reduce the effective adsorption capacity of the molecular sieve during repeated PSA cycles, thereby impairing the long-term oxygen production performance. Similar observations have been reported by Santos et al. (2008), who found that CO₂ contamination reduced the effective adsorption capacity of zeolite PSA beds because of competitive adsorption and incomplete regeneration.

To reduce CO₂-induced deterioration of the molecular sieve bed and maintain stable oxygen production, silica gel was packed at the bottom of the adsorption bed as a CO₂ guard layer. This configuration was designed to remove part of the CO₂ from the feed gas before it reached the main molecular sieve section. Figure 5 shows the variation in product-gas oxygen concentration with inlet CO₂ concentration under different silica gel loadings. Without a silica gel guard layer, the product-gas oxygen concentration gradually decreased as the inlet CO₂ concentration increased. Moreover, the decline became more pronounced at higher product-gas flow rates. At a product-gas flow rate of 1 L/min, increasing the inlet CO₂ concentration from 0 to 3% reduced the oxygen concentration by 2.9 percentage points. As the product-gas flow rate increased, the reduction in oxygen concentration became more pronounced. At a flow rate of 4 L/min, increasing the inlet CO₂ concentration from 0 to 3% resulted in a decrease of 8.9 percentage points in oxygen concentration. After silica gel was introduced into the adsorption bed, the decline in oxygen concentration was significantly suppressed, indicating that the guard layer effectively reduced the amount of CO₂ reaching the molecular sieve bed. When the silica gel loading was 50 g, the oxygen concentration remained nearly constant at a product-gas flow rate of 1 L/min. At product-gas flow rates of 2–3 L/min, the oxygen concentration decreased by 1.5 percentage points as the inlet CO₂ concentration increased from 0 to 3%. When the flow rate was further increased to 4 L/min, the decrease reached 4.2 percentage points, indicating that the protective effect of 50 g silica gel gradually weakened at higher flow rates. When the silica gel loading was increased to 150 g, no obvious decline in oxygen concentration was observed over the investigated flow-rate range of 1–4 L/min, indicating that the silica gel provided sufficient CO₂ adsorption capacity under the present operating conditions.

The results demonstrate that, at a constant product-gas flow rate, increasing the inlet CO₂ concentration led to a gradual decrease in oxygen concentration. Furthermore, the influence of CO₂ became more significant as the product-gas flow rate increased. After introducing silica gel, the decrease in oxygen concentration was effectively suppressed. Combined with the results presented in Fig. 4, these findings indicate that silica gel effectively removed CO₂ from the feed gas before it entered the molecular sieve bed. Consequently, competitive adsorption between CO₂ and N₂ was significantly reduced, thereby improving the resistance of the PSA oxygen generation system to CO₂-containing operating environments. Comparison of different silica gel loadings showed that increasing the amount of silica gel enhanced the CO₂ adsorption capacity of the guard layer, delayed CO₂ breakthrough, and further improved oxygen production stability. Therefore, incorporating a silica gel guard layer is an effective

strategy for maintaining stable oxygen production in PSA systems operating under CO₂-containing conditions. Similar guard-bed strategies have been reported in previous PSA studies, where strongly adsorbing impurities were removed before entering the main separation bed. The present results further demonstrate that adequate CO₂ pre-removal is essential for maintaining the long-term stability of PSA oxygen generation systems operating in confined environments.

3.3 Effect of CO on PSA Oxygen Production and Its Removal

3.3.1 Direct Separation of CO-Containing Air Using the PSA Oxygen Generation System

Experiments were first conducted to investigate the removal of CO by the PSA oxygen generation system without the addition of a CO oxidation catalyst in either the adsorption bed or the oxygen storage tank. Figure 6 presents the variations in CO concentrations in the product gas and desorption gas at different inlet CO concentrations and product-gas flow rates. As shown in Fig. 6, the PSA system removed approximately 94% of the inlet CO under all investigated operating conditions. Approximately 75–99% of the inlet CO was recovered in the desorption gas. The total amount of CO detected in the desorption gas and product gas was lower than the amount introduced into the feed gas. This result indicates that the molecular sieve possesses a certain adsorption capacity for CO. During PSA operation, part of the CO was retained within the molecular sieve bed through physical adsorption. Most of the adsorbed CO was subsequently released during the regeneration step. However, a small fraction of CO remained adsorbed after regeneration. As either the inlet CO concentration or the product-gas flow rate increased, the proportion of CO recovered in the desorption gas gradually decreased. In contrast, the CO concentration in the product gas increased. At relatively low inlet CO concentrations or low product-gas flow rates, the gas residence time in the adsorption bed was longer, allowing more complete adsorption of CO by the molecular sieve. Consequently, less CO escaped into the product gas. At higher inlet CO concentrations or higher product-gas flow rates, the mass transfer zone gradually approached the outlet of the adsorption bed. As a result, CO breakthrough occurred earlier and a larger amount of CO appeared in the product gas. Meanwhile, incomplete regeneration resulted in a larger amount of residual CO remaining inside the adsorption bed after each PSA cycle.

Overall, the results demonstrate that the molecular sieve possesses a measurable adsorption capacity for CO. Part of the adsorbed CO could be released during regeneration, whereas another fraction remained adsorbed inside the bed. As the adsorption bed gradually approached saturation, the amount of CO detected in the product gas increased. Because the total CO recovered from the product gas and desorption gas was lower than the inlet amount, part of the CO was retained within the molecular sieve after regeneration.

These results indicate that PSA alone cannot completely eliminate CO from the product gas under the investigated operating conditions. A small amount of CO still penetrated the adsorption bed and appeared in the product gas. This CO concentration does not satisfy the safety requirements for medical oxygen. Therefore, an additional catalytic oxidation process is required to completely remove residual CO from the PSA product gas before medical use. Therefore, PSA should primarily be regarded as a pre-concentration step for CO removal, whereas complete purification requires a downstream catalytic oxidation unit. This finding provides the basis for the subsequent investigation of Hopcalite catalyst performance presented in Section 3.3.2.

3.3.2 Room-Temperature Catalytic Removal of CO

To evaluate the room-temperature catalytic performance of the CO oxidation catalyst, experiments were conducted under different humidity conditions. Figure 7 shows the variations in product-gas CO concentration and relative humidity with operating time for different material configurations. Three material configurations were designed according to the arrangement of desiccant and CO catalyst in the oxygen storage tank. In Scheme A, the oxygen storage tank was filled with 100 g of CO catalyst. In Scheme B, 50 g of desiccant was placed upstream of 100 g of CO catalyst. In Scheme C, the desiccant loading was increased to 100 g while the catalyst loading remained at 100 g. Each experiment was carried out continuously for 90 min. As shown in Fig. 7, Scheme A exhibited the highest product-gas humidity, which gradually increased throughout the experiment. However, the product-gas humidity remained lower than the inlet humidity throughout the experiment. The CO concentration in the product gas increased gradually with operating time, and the increase became more pronounced after prolonged operation. Compared with Scheme A, Scheme B maintained a lower product-gas humidity and exhibited a much slower increase in CO concentration. Scheme C maintained the lowest product-gas humidity throughout the experiment. In Scheme C, the product-gas humidity remained the lowest, and no detectable CO was observed in the product gas during the entire experiment. Comparison of the three configurations demonstrates that the catalyst effectively oxidized CO at room temperature. The absence of CO in the initial stage of Schemes A and B indicates that the catalyst exhibited excellent initial activity. However, its catalytic performance gradually deteriorated as moisture accumulated during continuous operation.

The lower humidity observed in the product gas indicates that part of the water vapor was adsorbed by the catalyst bed. The gradual increase in CO concentration with operating time indicates progressive catalyst deactivation caused by water adsorption. This observation is consistent with the findings of Jiang et al. (2017), who reported that the activity of Hopcalite catalysts gradually decreases under humid operating conditions. Water molecules compete with CO for the active Cu–Mn oxide sites and block the redox cycle responsible for CO oxidation, thereby suppressing catalytic activity (Vepřek et al. 1986). Because the humidity entering the catalyst bed was reduced in Scheme B, catalyst deactivation was alleviated and the CO concentration in the product gas remained much lower than that in Scheme A. In Scheme C, the larger amount of desiccant further reduced the humidity entering the catalyst bed. Consequently, the catalyst maintained stable activity throughout the experiment, and no detectable CO

appeared in the product gas. These results demonstrate that maintaining a low-humidity environment is essential for sustaining the room-temperature activity of Hopcalite catalysts and achieving complete CO removal. Therefore, a dehydration unit should be installed upstream of the CO catalyst in practical PSA oxygen generation systems to prevent moisture-induced catalyst deactivation and ensure long-term CO removal efficiency.

3.3.3 Effect of Catalyst Position on CO Removal

Table 2
Adsorption-Bed Configurations Used to Evaluate Catalyst Position

Bed layer	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
L1	ZMS 184.5 mm	ZMS 149 mm	ZMS 78 mm	Catalyst 35.5 mm	ZMS 184.5 mm	ZMS 184.5 mm
L2			Catalyst 35.5 mm	ZMS 149 mm		
L3		Catalyst, 35.5 mm	ZMS 71 mm			
L4	Activated-Al ₂ O ₃ 35.5 mm	Activated-Al ₂ O ₃ 35.5 mm	Activated-Al ₂ O ₃ 35.5 mm	Activated-Al ₂ O ₃ 35.5 mm	Activated-Al ₂ O ₃ 35.5 mm	Activated-Al ₂ O ₃ 35.5 mm
L5	/	/	/	/	ZMS 56.8 mm	ZMS 21.3 mm
L6	/	/	/	/	Catalyst 35.5 mm	Catalyst 71 mm

The previous experiments demonstrated that efficient CO oxidation at room temperature requires both a low-humidity gas stream and an appropriate catalyst location. Activated alumina and the molecular sieve effectively remove water vapor from the feed gas, providing a relatively dry environment for the downstream catalyst regardless of whether the catalyst is installed in the adsorption bed or the oxygen storage tank. Figure 8 and Table 2 respectively show the schematic diagrams of the filling positions and filling schemes of the molecular sieves, activated Al₂O₃ and the catalysts. Figure 9 compares the product-gas CO concentration for different composition locations and composition loadings. As expected, the highest CO concentration was observed in the absence of a catalyst layer. When the catalyst was installed inside the adsorption bed, the product-gas CO concentration gradually decreased as the catalyst position moved from the bottom to the top of the bed. For the same catalyst loading, placing the catalyst in the oxygen storage tank produced a substantially lower CO concentration than

placing it inside the adsorption bed. Under an inlet CO concentration of 1000 ppm, only 2 ppm of CO was detected in the product gas. Increasing the catalyst loading in the oxygen storage tank to the same amount as that used in the adsorption beds resulted in no detectable CO in the product gas.

For the same catalyst loading, positioning the catalyst closer to the product-gas outlet resulted in lower CO concentrations in the product gas. This can be attributed to the higher oxygen concentration in the downstream section of the PSA process, which favors the catalytic oxidation of CO. Consequently, the catalyst located near the product-gas outlet operated under more favorable oxidation conditions. In addition, the gas residence time inside the catalyst bed is another critical factor affecting catalytic performance. As the gas passed through the adsorption bed, nitrogen was continuously adsorbed, resulting in a gradual decrease in gas flow rate. Because the bed cross-sectional area remained constant, the reduction in gas flow correspondingly reduced the superficial gas velocity. After entering the oxygen storage tank, the gas velocity decreased even further while maintaining a high oxygen concentration. These conditions provided the most favorable environment for catalytic CO oxidation. The lower gas velocity increased the residence time of the gas inside the catalyst bed, thereby improving the contact efficiency between CO molecules and catalytic active sites and promoting more complete CO oxidation. Therefore, for the same catalyst loading, the CO removal performance followed the order: bottom of the adsorption bed < middle of the adsorption bed < top of the adsorption bed < oxygen storage tank. These results demonstrate that placing the catalyst in the oxygen storage tank is the most effective configuration for CO removal because it combines a high oxygen concentration with a low gas velocity and a long gas residence time. From an engineering perspective, installing the catalyst in the oxygen storage tank not only improves CO removal efficiency but also simplifies the internal structure of the adsorption bed, making the configuration more suitable for practical PSA oxygen generation systems.

3.3.4 Effect of Gas Hourly Space Velocity on CO Removal in the Oxygen Storage Tank

Gas hourly space velocity (GHSV) is one of the key operating parameters affecting the catalytic performance of the CO oxidation catalyst. Figure 10a illustrates the effect of GHSV on CO removal performance under different inlet CO concentrations. As shown in Fig. 10a, the CO concentration in the product gas increased with increasing GHSV. This behavior is attributed to the shorter gas residence time within the catalyst bed at higher GHSV, which reduced the contact time between CO molecules and catalytic active sites and resulted in incomplete CO oxidation (Jia et al. 2014). The maximum GHSV that achieved complete CO conversion depended on the inlet CO concentration. Complete CO removal was achieved over the entire investigated GHSV range when the inlet CO concentration was 200 ppm. When the GHSV was lower than 1130 h^{-1} , complete CO removal was achieved for inlet CO concentrations up to 1000 ppm.

Lower GHSV generally improved CO conversion efficiency. However, excessively low GHSV requires either a larger catalyst bed or a lower product-gas flow rate, both of which reduce system compactness

and productivity. Therefore, the highest GHSV that still resulted in zero CO concentration in the product gas was defined as the optimum GHSV for a given inlet CO concentration. The optimum GHSV values obtained at different inlet CO concentrations were fitted using a power-law relationship, as shown in Fig. 10b. The equation of the fitted curve in the figure is:

$$y = 548923.25 \times x^{-0.9}$$

2

where y is the optimum GHSV (h^{-1}), and x is the inlet CO concentration (ppm). The fitted equation accurately described the variation in optimum GHSV with inlet CO concentration. The optimum GHSV decreased progressively as the inlet CO concentration increased. At a constant product-gas flow rate, increasing the inlet CO concentration increased the number of CO molecules entering the catalyst bed per unit time. Consequently, a lower GHSV (i.e., a longer residence time) was required to provide sufficient contact between CO molecules and catalytic active sites for complete oxidation. These results provide practical guidance for catalyst design in PSA oxygen generation systems. By selecting an appropriate GHSV according to the expected inlet CO concentration, complete CO removal can be achieved while minimizing catalyst volume and pressure drop. The empirical relationship obtained in this study may therefore serve as a useful reference for the engineering design and scale-up of integrated PSA oxygen generation systems.

4. Conclusions

This study systematically investigated the effects of humidity, CO_2 , and CO on PSA oxygen generation and proposed corresponding purification strategies for improving the performance of PSA oxygen generation systems in complex gas environments. The main conclusions are summarized as follows:

1. Water vapor significantly deteriorated the oxygen production performance of the PSA system because of competitive adsorption on the zeolite molecular sieve. As the relative humidity increased from 50% to 80%, the oxygen concentration decreased by 2.9 percentage points when the activated alumina-to-molecular sieve ratio was 1:5. Increasing the activated alumina loading effectively protected the molecular sieve from moisture, and no obvious decline in oxygen concentration was observed at a ratio of 1:1, demonstrating that a sufficient dehydration layer is essential for stable PSA oxygen production under humid conditions.
2. CO_2 was preferentially adsorbed by the molecular sieve and gradually reduced its effective nitrogen working capacity. As the inlet CO_2 concentration increased from 0 to 3%, the oxygen concentration decreased from 92.4% to 90.2%. Introducing a silica gel guard layer effectively reduced the amount of CO_2 entering the molecular sieve bed. When 150 g of silica gel was used, no significant decrease in oxygen concentration was observed at oxygen production flow rates of $1\text{--}4\text{ L min}^{-1}$, indicating that feed-gas pretreatment is an effective strategy for improving the CO_2 tolerance of PSA oxygen generation systems.

3. The PSA process alone could not completely remove CO from the feed gas, although approximately 94% of the inlet CO was removed by adsorption. A small amount of residual CO remained in the product gas because of incomplete adsorption and regeneration. Under room-temperature conditions, the Hopcalite catalyst effectively oxidized the remaining CO, while its activity gradually decreased in humid environments because water molecules occupied the catalytic active sites.
4. Catalyst configuration had a significant influence on CO removal performance. For the same catalyst loading, placing the catalyst in the oxygen storage tank achieved the best purification performance because of the combined effects of higher oxygen concentration, lower gas velocity, and longer gas residence time. Furthermore, the optimum gas hourly space velocity (GHSV) decreased with increasing inlet CO concentration, and the relationship was successfully described by an empirical equation.

Declarations

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Author Contribution

Ye Li: Writing - original draft, Writing - review & editing, Methodology, Data curation Investigation. Jianqiu Bei: Writing - original draft, Methodology, Data curation. Ziyi Li : Supervision, Resources. Quanli Zhang: Conceptualization, Data curation, Writing - review & editing, Investigation. Yingshu Liu: Writing - review & editing, Investigation, Funding acquisition. Ningqi Sun: Writing - review & editing, Validation. Chuanshao Zhang: Writing - review & editing, Validation. Shifeng Wang: Investigation, Resources. Xiong Yang: Validation, Writing - review & editing, Funding acquisition.

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Figures

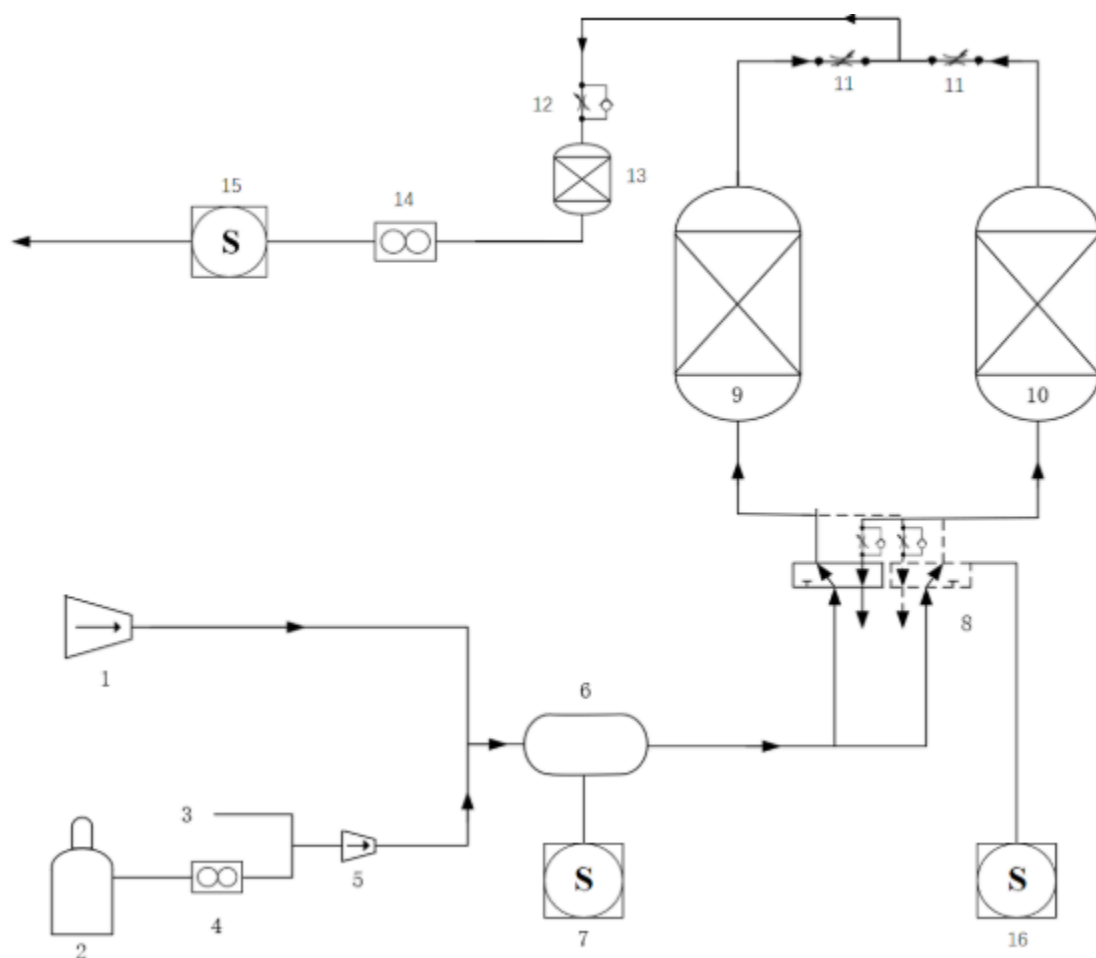


Figure 1

Process flow diagram of the experimental PSA oxygen-generation system: 1, compressor A; 2, gas cylinder; 3, steam generator; 4 and 14, mass flowmeters; 5, compressor B; 6, buffer tank; 7, 15, and 16, CO analyzers; 8, combination valve; 9, adsorption bed A; 10, adsorption bed B; 11, restrictor; 12, check valve; and 13, oxygen storage tank.

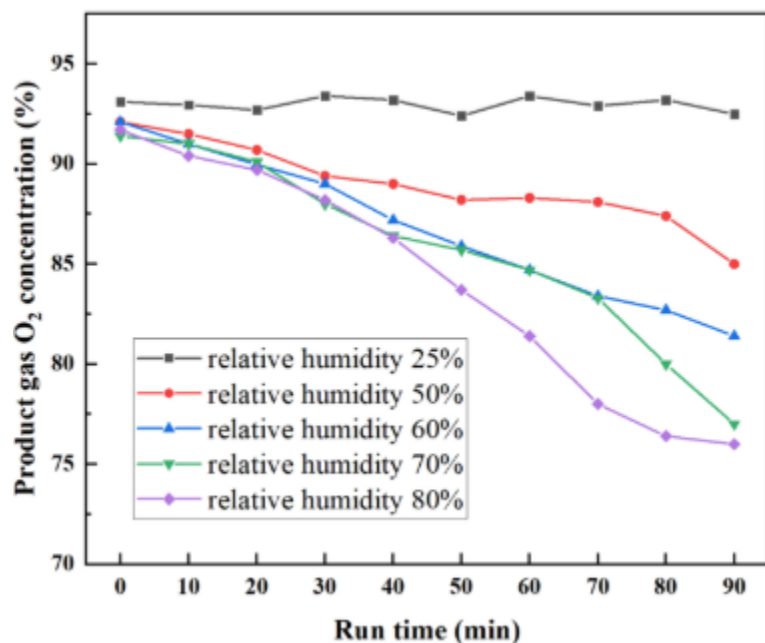


Figure 2

Effect of feed-gas relative humidity on product-gas oxygen concentration during 90 min of PSA operation.

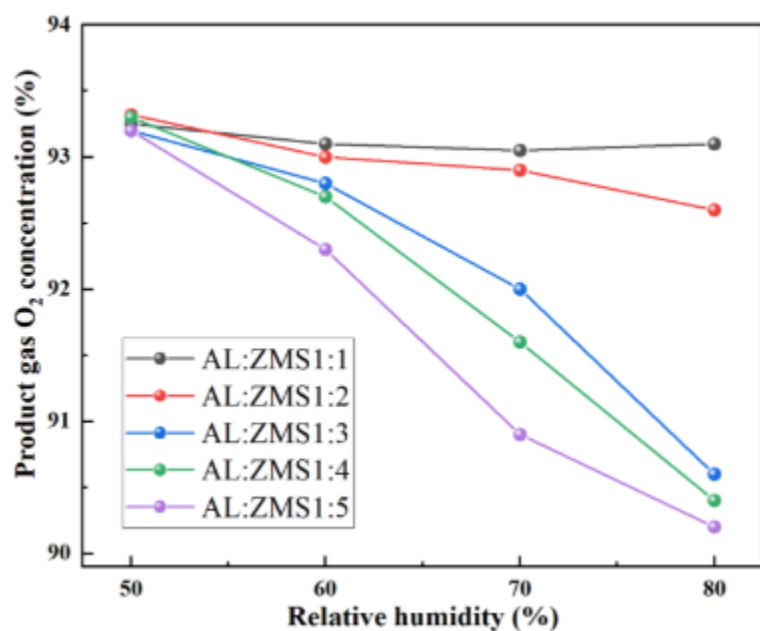


Figure 3

Effect of activated alumina-to-molecular sieve mass ratio on product-gas oxygen concentration at different relative humidities.

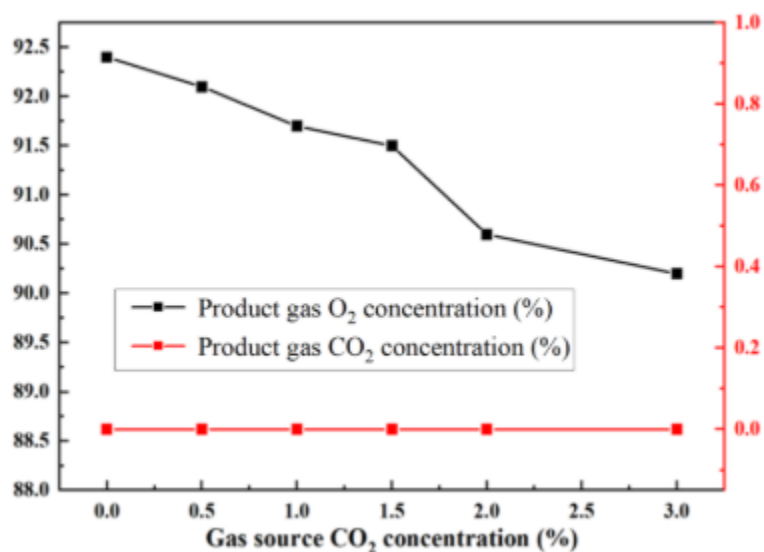


Figure 4

Effect of inlet CO₂ concentration on product-gas oxygen and CO₂ concentrations.

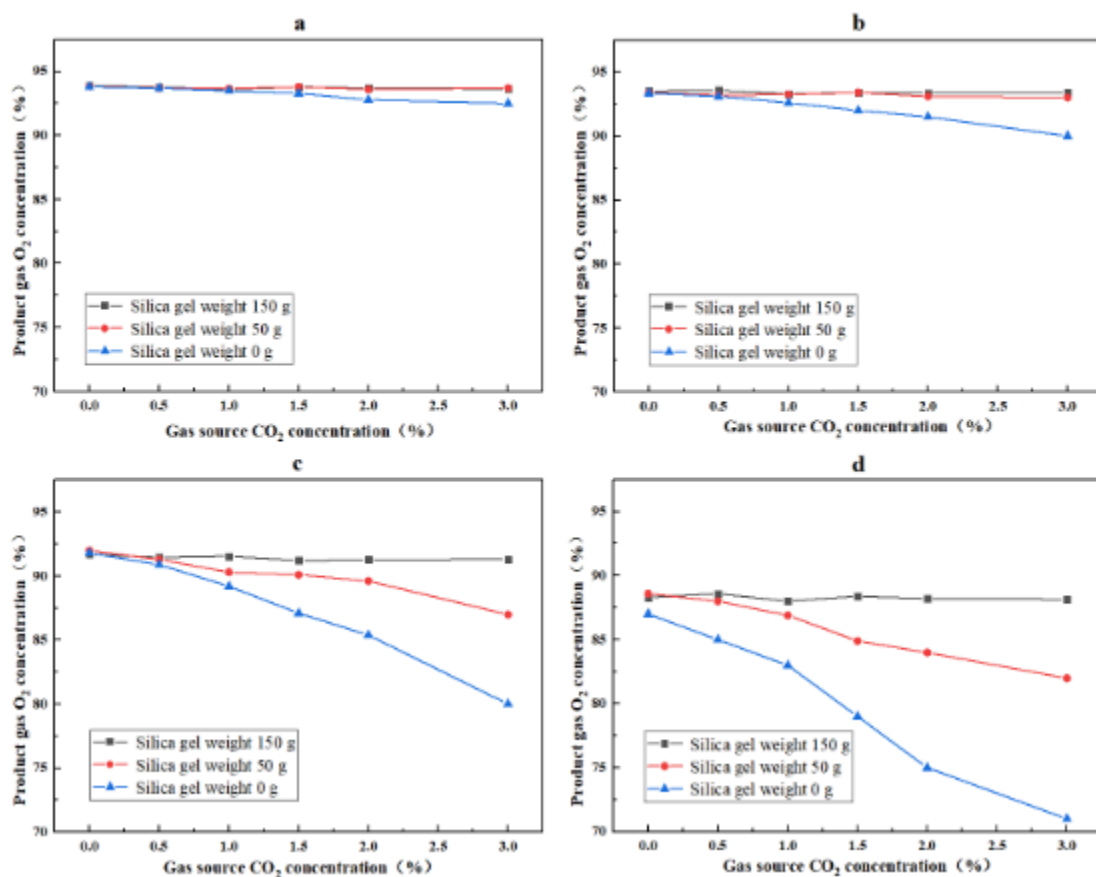


Figure 5

Effect of inlet CO₂ concentration and silica gel loading on product-gas oxygen concentration at product-gas flow rates of (a) 1, (b) 2, (c) 3, and (d) 4 L/min.

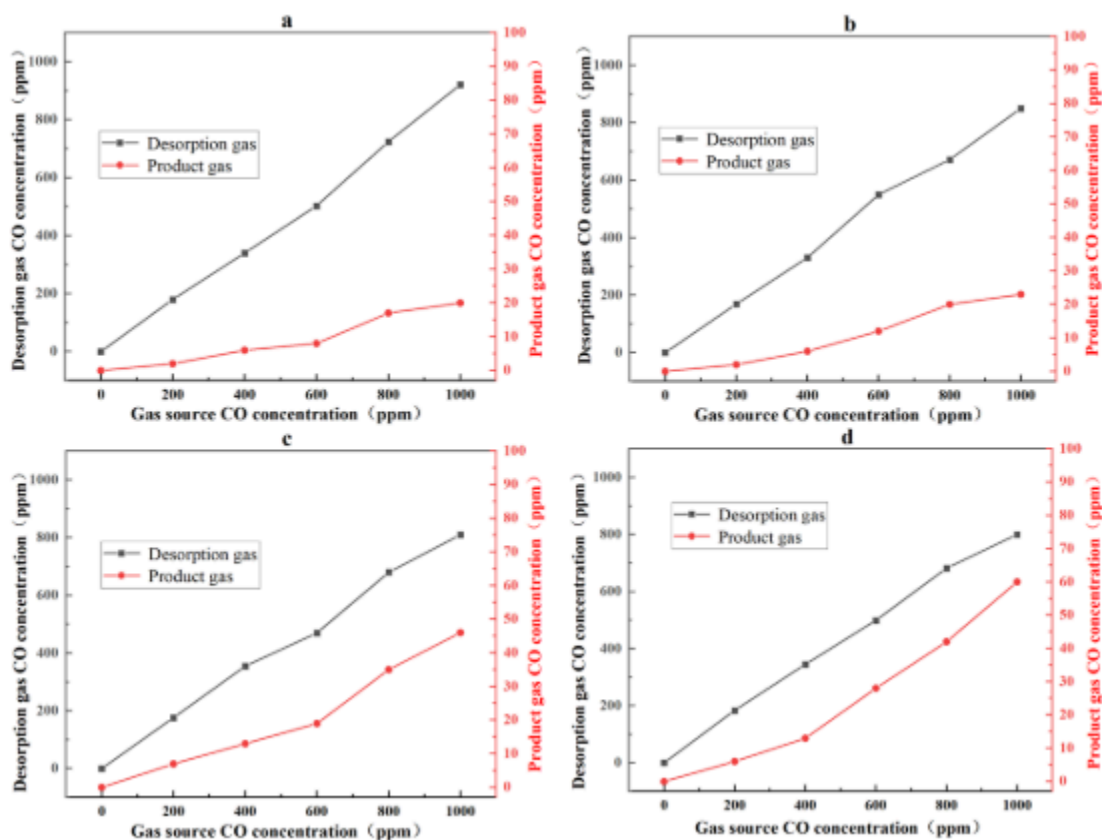


Figure 6

CO concentrations in the desorption gas and product gas as functions of inlet CO concentration at product-gas flow rates of (a) 2.0, (b) 2.5, (c) 3.0, and (d) 3.5 L/min.

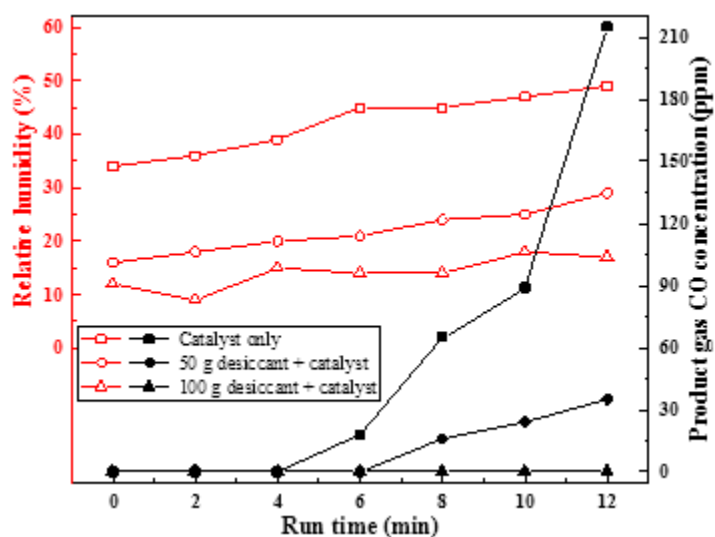


Figure 7

CO concentrations in the desorption gas and product gas as functions of inlet CO concentration at product-gas flow rates of (a) 2.0, (b) 2.5, (c) 3.0, and (d) 3.5 L/min.

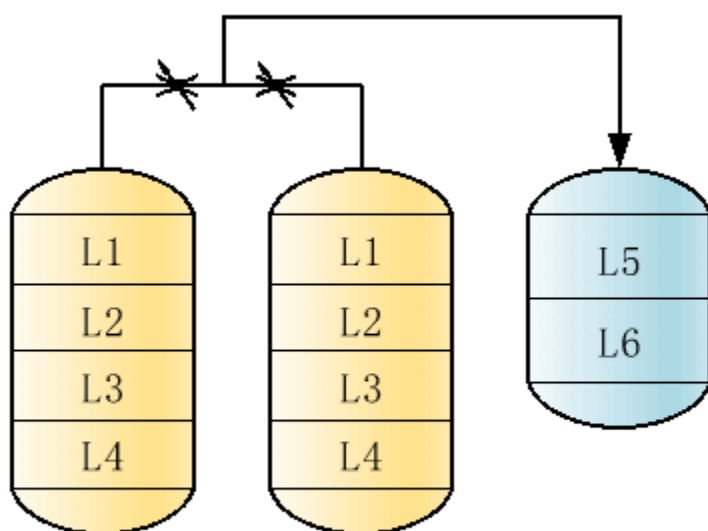


Figure 8

Schematic locations of layers L1-L4 in the two adsorption beds and layers L5-L6 in the oxygen storage tank.

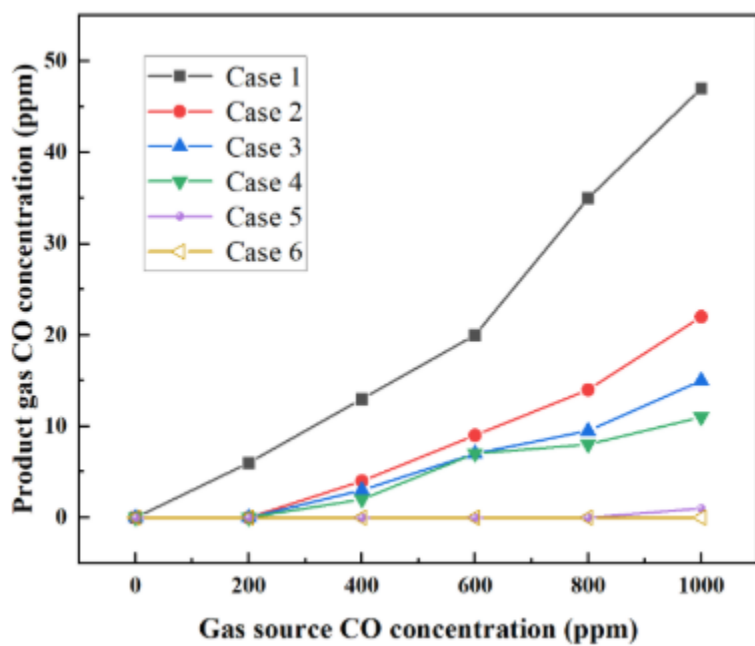


Figure 9

Effect of catalyst position and loading on product-gas CO concentration.

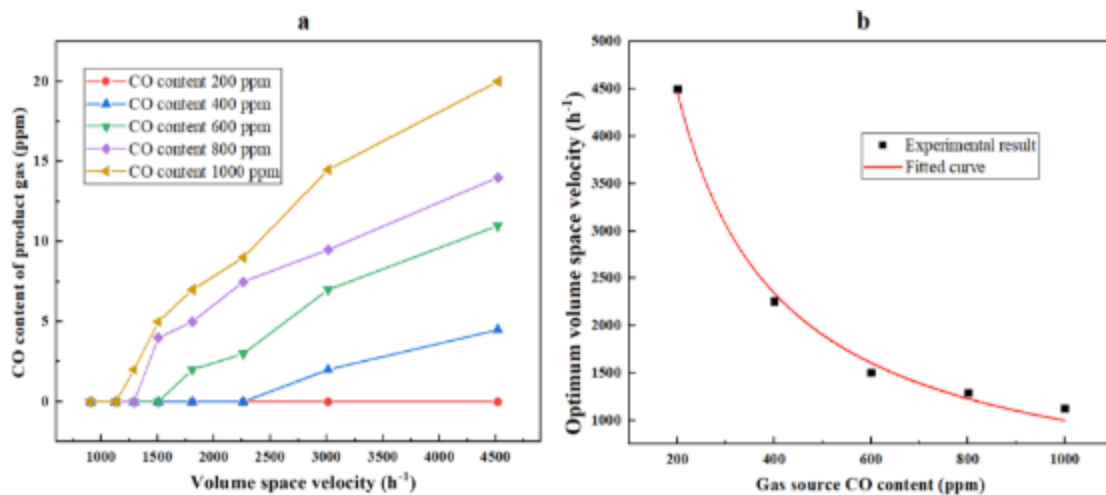


Figure 10

Effect of gas hourly space velocity on outlet CO concentration and determination of the optimum space velocity at different inlet CO concentrations: (a) outlet CO concentration as a function of gas hourly space velocity; (b) relationship between the optimum gas hourly space velocity and inlet CO concentration.