

Review Article

Overview of CO₂ Capture from Flue Gas Streams by Vacuum Pressure Swing Adsorption Technology

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Abstract

With increasing concerns about CO₂ emissions and their impact on global warming, CO₂ capture technologies have been widely studied. Adsorption technology, as an important process for gas separation, has also been studied for CO₂ capture from flue gas for more than two decades. Because the pressure of most flue gas streams is approximately atmospheric, vacuum swing adsorption process (VSA) is preferred. This paper provides an overview of the development of VSA processes for CO₂ capture based on commercial adsorbent materials. We discuss the general trends in process performance with respect to adsorbent characteristics, cycle design and operating conditions. We have also discussed the impact of impurities in feed gases on VSA processes and strategies for dealing with the negative impacts. Finally, energy consumption in CO₂VSA processes is summarized. The review of process performance is mainly based on simulation and laboratory scale work.

Keywords: CO₂ capture; Vacuum swing adsorption; TSA

Introduction

CO₂ is a major greenhouse gas and hence, contributes significantly to global warming. The development and deployment of CCS (CO₂ capture and storage) technologies is considered the most important option to make much deeper cuts in greenhouse gas emissions, and CO₂ concentration of greater than 95% is commonly required for sequestration [1]. Currently three major separation technologies namely absorption, membranes and adsorption are being developed to capture and concentrate CO₂ from flue gases for CSS applications [2, 3]. Absorption is the most mature of these technologies, and has long been used for CO₂ capture, though not from power plants. However, it results in high energy consumption during the high temperature absorbent regeneration [4].

Adsorption technology is increasingly becoming popular for CO₂ capture because of its potential low energy consumption, simple operation, easy maintenance and flexibility in design to meet different demand requirements [5-7]. Each of the different adsorption processes such as TSA (temperature swing adsorption), PSA (pressure swing adsorption), VSA (vacuum swing adsorption), and ESA (electrical swing adsorption) may be most suitable for treating feed gases with different CO₂ concentrations [8]. The TSA can be designed to directly utilize cheaper, low-grade thermal energy resources from power plants for regeneration to reduce the operating cost. However, the longer time required for heating/cooling limits its application for CO₂ capture. With the long cycle time, productivity will be lower compared to other adsorption technologies. The product may also be diluted by the purge gas if regeneration is performed by direct hot gas purge as used in conventional systems [9-12]. Because the pressure in flue gas streams is approximately equal to 1.0 bar and CO₂ concentration in the feed gas is commonly higher than 10%, VSA is considered more economical for CO₂ capture than PSA (where significant compression of the feed gas is required) [13,14]. The temperature range of flue gases varies by their sources and pre-treatment processes that may

be available. Taking a typical coal-based power plant for instance, the flue gas stream may be available at a temperature ranging from 30 to 80°C or even higher, depending on the extent of heat recovery from the stream [15]. The VSA performance is sensitive to the feed gas temperature, so a further heat treatment may be required to condition the flue gas before feeding it to the VSA plant, which will inevitably impact on the separation efficiency and economics of the process.

Adsorbents play a key role in adsorption technology. The adsorbent determines the overall CO₂ capture performance in VSA technology [16,17]. The key elements for a good adsorbent in CO₂VSA technology are high selectivity of CO₂ over N₂, high adsorption capacity of CO₂, rapid adsorption/desorption kinetics, stable adsorption capacity after repeated cycles, and adequate mechanical strength of the particles [18]. Many adsorbents with high CO₂ adsorption capacity and selectivity have been developed recently such as MOFs, amine modified adsorbents, etc. [19]. While the number of new adsorbent materials reported has proliferated, only a very select few will undergo bench-top testing and even fewer will pass on to pilot testing stage, partly due to limited availability of production materials since large scale production is often not the goal of initial materials research. Therefore, VSA process design for CO₂ capture still focuses on commercially available materials such as zeolites, activated carbon and CMS which can be purchased in bulk and tested in pilot or field installations [20-24]. This paper provides a review of VSA process development for CO₂ capture, and specifically discusses how adsorbent characteristics, process design and operating conditions impact the overall process performance.

Commercial CO₂ Adsorbents

In capture processes of CO₂ from flue gas streams, it is assumed that the impurities in the feed gases including water are removed through flue gas pre-treatment processes so that CO₂ separation from flue gases can be represented as that from a mixture of CO₂ and N₂,

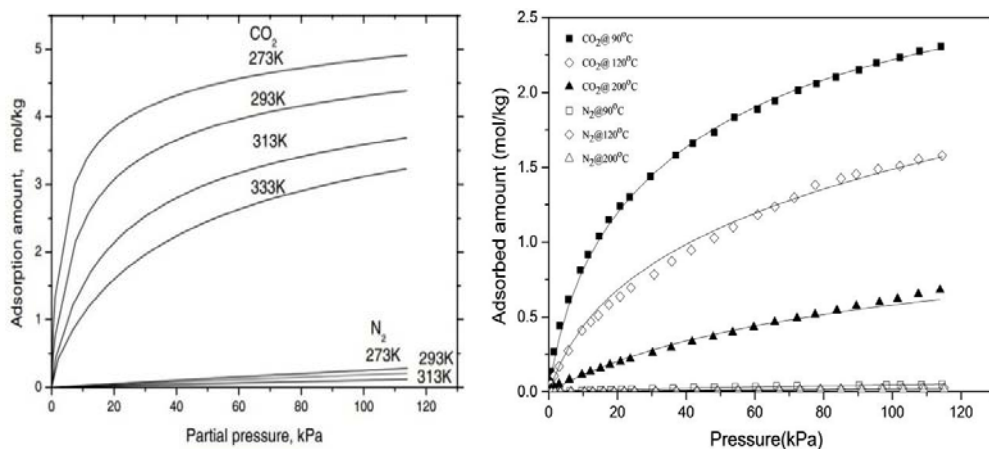


Figure 1: Isotherms of CO₂ and N₂ on zeolite 13X at low temperature [22](left) and high temperature [30](right).

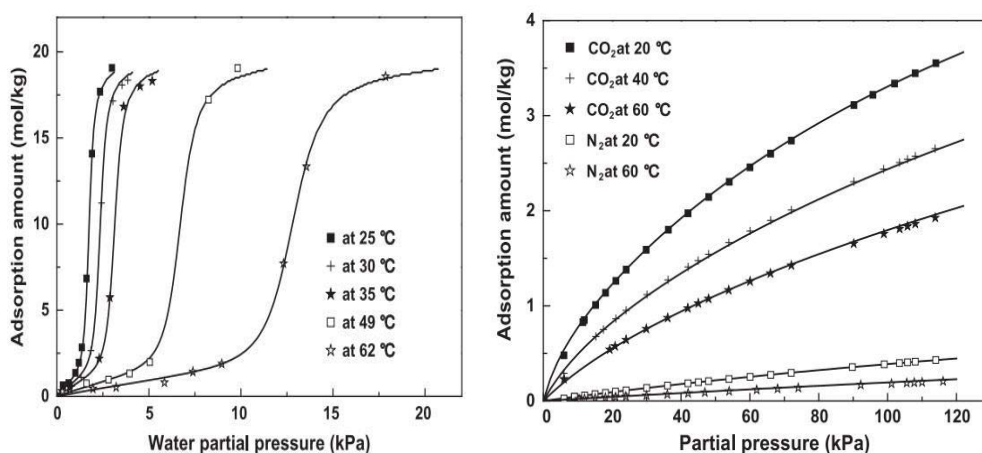


Figure 2: Isotherms of water vapor and CO₂ on activated carbon [32]: water vapor (left) and CO₂ (right).

Zeolite materials have been widely studied for CO₂ capture from flue gases in fossil fuel power plants, natural gas and biogas facilities [5,14,25,26]. According to the literature on CO₂ capture using different types of natural and various types of synthetic zeolites such as Y, X, A, 13X zeolite shows superior performance for CO₂ separation from N₂ at relatively low temperatures [27]. Some researchers have considered 5A in TSA processes because of its higher volumetric capacity and high working capacity between low and high temperatures [28,29]. Zeolite 13X, studied for more than two decades, is the benchmark material for CO₂VSA systems because of its high working capacity and selectivity for CO₂ at the prevailing conditions of the process. From the isotherms of CO₂ and N₂ on 13X [22,30], both CO₂ and N₂ adsorption amount increases as their partial pressures increase (Figure 1) in the usual way as expected for a physisorbent. As the temperature increases, the adsorption amount for both CO₂ and N₂ decreases, indicative of exothermic adsorption. Although 13X is a physisorbent for CO₂ and as such should be restricted to modest temperature application, we have found that it presents a relatively high CO₂ working capacity even over 120°C. Therefore, it is an ideal adsorbent for CO₂ and N₂ separation as it has a wide operating temperature range.

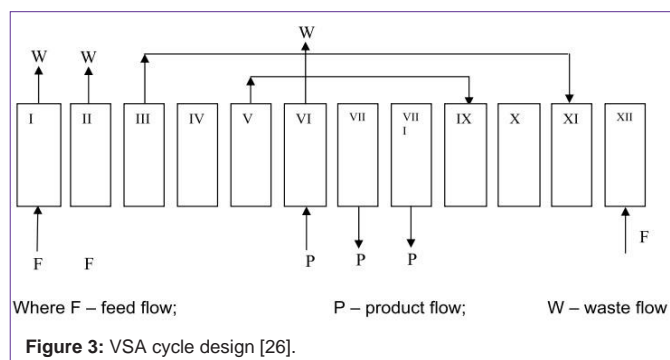
CO₂ adsorption capacity on 13X is reduced significantly by water

vapor because water is strongly adsorbed onto the hydrophilic sodium cations within the supercage, displacing sites for CO₂ adsorption. As a result, a guard layer must be employed to avoid moisture contamination of 13X zeolite. Traditional activated carbon is also a commonly used adsorbent for CO₂ adsorption but contains both hydrophobic and hydrophilic sites on its surface. Water vapor can be adsorbed onto the surface by hydrogen bonding to the surface functional groups. However, this bonding is very weak so that the water vapor can be removed by reducing its partial pressure and as a result activated carbons are often regarded as more suitable for wet flue gas treatment [31]. The isotherms of water vapor and CO₂ on activated carbon are shown in (Figure 2) [32]. CO₂ adsorption capacity on activated carbon is much lower compared to that of zeolite 13X. However, its ability to moderately withstand water vapor makes it a promising material in the application of CO₂ capture from wet (real) flue gases. Current research is focused on modifying the activated carbon surface with desired functional groups in order to improve its CO₂ adsorption capacity and selectivity [33, 34].

VSA Process Development

Cycle design

There are basic five steps employed in most VSA process designs



[21,26], which include adsorption, desorption, re-pressurization, pressure equalization and product purge (Figure 3). In the adsorption step, CO₂ is adsorbed onto the adsorbent packed in the column as the feed gas (flue gas) passes through the column, while CO₂-lean gas stream exits to the atmosphere. The amount of CO₂ adsorption depends on the operating pressure and temperature. In the desorption step, the adsorbed CO₂ is desorbed from the bed and extracted into a CO₂-rich gas phase by reducing the pressure to vacuum (or sub-atmospheric) levels. In the re-pressurization step, feed gas or part of the CO₂-lean gas is used to pressurize the adsorption bed, from the bottom or top of the bed, until the pressure in the bed is equal to that in the feed step for the next cycle. Pressure equalization is used in multiple-bed VSA systems. A bed at higher pressure (usually after adsorption) transfers gas to a bed at lower pressure (after vacuum desorption) until their pressures equalize. This can bring energy savings by reducing the amount of re-pressurization required by the low-pressure bed, and also improve CO₂ product purity. For product purge, part of the extracted product or a CO₂-rich gas is used to purge the bed before the desorption step. However, in order to obtain high CO₂ product purity, the pressure at the top of the bed needs to be controlled to the same pressure as in the last equalization step. Because CO₂ adsorption capacity is much higher than N₂, most N₂ trapped in the void spaces of the adsorbent or adsorbed in the bed can be displaced by the purge gas, leading to a more pure CO₂ product in the subsequent vacuum desorption step.

A light reflux step can also be included in the cycle design [35], but this step must be carefully controlled to avoid breakthrough of the nitrogen into the CO₂ product since the proportionate pattern

profile in this step will lead to rapid N₂ propagation. CO₂ adsorption on zeolite 13X is much stronger (and non-linear) than N₂ so that the light refluxes gas flow (a N₂-rich gas stream) cannot easily clean the CO₂ front but rather dilutes the final CO₂ product.

Rapid-swing adsorption, characterized by faster cycling permits the adsorbent to be used more frequently and, therefore, leads to CO₂ productivity and relatively smaller plant sizes. However, recoveries may be lower due to kinetic limitations. It is often used in O₂ concentrators, where high purity and/or recovery rate is not essential and feed gas can be discarded without concern [36]. Therefore, this is not discussed further in this review.

Operating parameters in CO₂ VSA processes

Optimizing operating parameters is important for the VSA process to achieve satisfactory performance. Pressure and temperature are the major operating parameters, and affect CO₂ product purity and recovery by changing working capacity. CO₂ working capacity (WC) and selectivity (S) can be estimated from isotherm of single component on adsorbent by equations 1, 2 and 3 below:

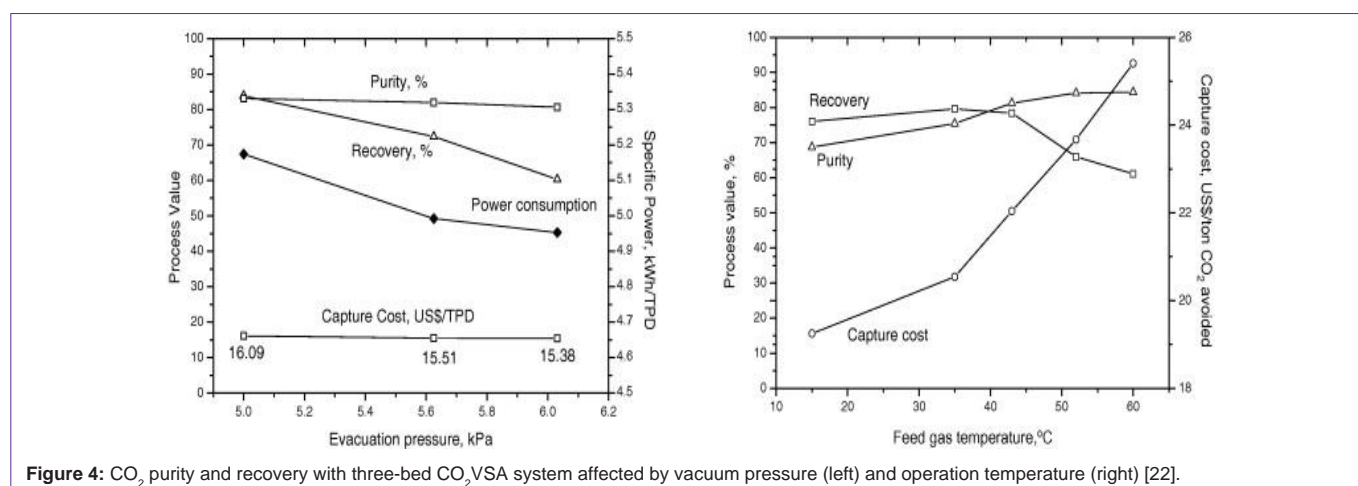
$$WC \text{ (mol/kg)} = CO_{2PH} - CO_{2PL} \quad (1)$$

$$S_{WC} = WC_{CO_2} / WC_{N_2} \quad (2)$$

$$S = CO_{2PH} / N_{2PH} \quad (3)$$

Where WC is CO₂ working capacity and S is CO₂ selectivity; CO_{2PH} is the amount of CO₂ that is adsorbed at the highest CO₂ partial pressure (i.e. CO₂ partial pressure in the feed) and CO_{2PL} is the amount of CO₂ that is adsorbed at the lowest CO₂ partial pressure (i.e. CO₂ partial pressure reached at the end of desorption); S_{WC} is the selectivity for working capacity of CO₂ and N₂. Although selectivity S is often used to assess adsorbent performance, selectivity based on working capacity is a more accurate assessment metric.

As working capacity varies with CO₂ partial pressure, higher pressure at the same CO₂ concentration in feed gas will result in an increase of CO₂ adsorption in the bed. However, more energy will be required for compressing the feed gas. Therefore, most studies are conducted for constant pressure feed steps. The pressures at the end of vacuum desorption and equalization is most important in VSA testing as shown in Figure 4. During the pressure equalization step, some of the CO₂ adsorbed in the sorbent can be released into



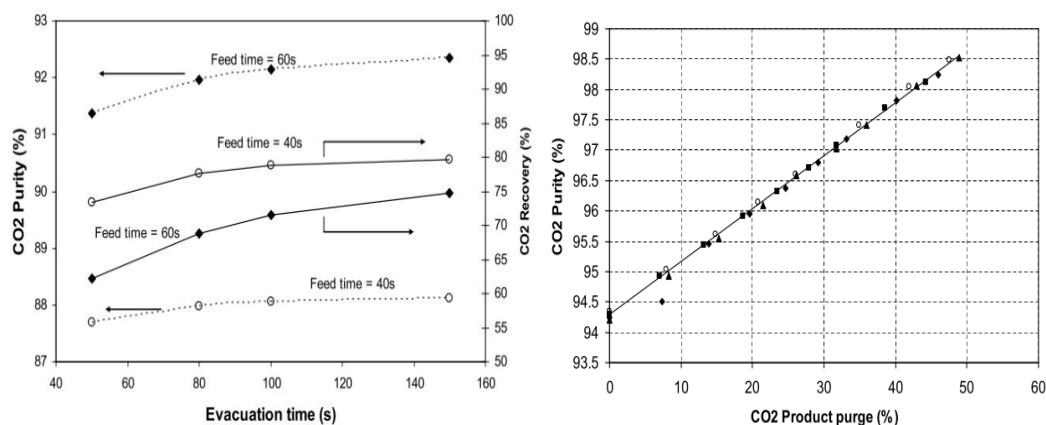


Figure 5: CO₂VSA performance affected by flow-rates and CO₂ product percentage [26].

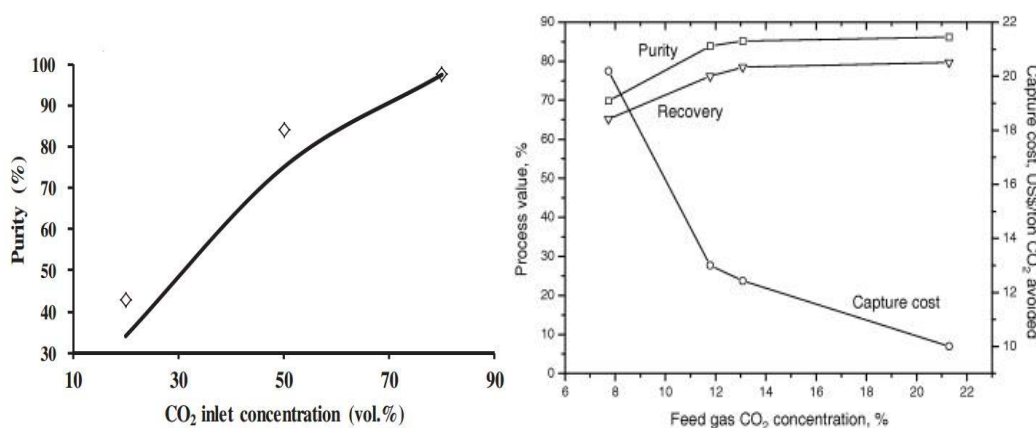


Figure 6: CO₂VSA performance at varying CO₂ inlet concentration [22,43].

the gas phase so that N₂ in the void spaces of the bed ahead of the CO₂ front or even some co-adsorbed N₂ can eluted from the bed (which is transferred onto another bed). Thus, after several pressure equalizations, S_{wc} will increase, leading to increase in CO₂ product purity [26]. At the same time, the pressure in the bed (before the evacuation step) will decrease, which means the vacuum pump will perform less work during desorption, and this can bring some amount of energy savings. The vacuum pressure applied is very important and it affects both CO₂ purity and recovery. Many previous studies [22,26,35,37], have shown that deep vacuum levels are needed to achieve high recoveries and purities for CO₂ capture from post-combustion flue gas streams. However, the deeper vacuum requires multistage pump units which can be very expensive and also consume much power. The deep vacuum also results in very large suction and valve line sizes [38].

Temperature is another important parameter in the VSA system as shown in Figure 4. For zeolite 13X (Figure 1), CO₂ working capacity varies at different temperatures: the working capacity is 0.35mol/kg at 0°C as CO₂ partial pressure changes from 15kPa to 10kPa, but 0.4mol/kg at 40°C and 0.35mol/kg at 60°C. Selectivity normally increases as temperature increases in the temperature range from 40 to 90°C on zeolite 13X. Therefore, CO₂ purity in CO₂ product increases as the operation temperature increases, which is confirmed by our experiments (Figure 4).

Flow-rates in the feeding and desorption steps are also important. Firstly, a high flow-rate will cause large pressure drop (Δp) which can be described by the Ergun equation [39] (equation 4):

$$-\frac{\Delta P}{L} = \frac{150\mu(1-\varepsilon)^2 u_0}{\varepsilon^3 d_p^2} + \frac{1.75(1-\varepsilon)\rho u_0^2}{\varepsilon^3 d_p} \quad (4)$$

Where L is the height of the bed, μ is the fluid viscosity ε is the void space of the bed, u_0 is the fluid superficial velocity, d_p is the partial diameter and ρ is the density of the fluid.

The pressure drop increases as the velocity increases, which will affect CO₂ adsorption and also desorption. Higher pressure is required to overcome the pressure drop for the feed gas to reach a higher flow-rate and the pressure drop also causes insufficient vacuum level at the top of bed during desorption step so that adsorbed CO₂ cannot be desorbed effectively. The flow-rate also impacts adsorption/desorption kinetics. CO₂ adsorption on 13X beads is macropore diffusion controlled, both under Knudsen and molecular diffusion regimes [40]. Thus, the flow-rate will affect CO₂ recovery during VSA process as well (Figure 5 left). The data in Figure 5 left were obtained by fixing the level of vacuum pressure reached at the end of desorption, while varying desorption time, so that velocity decreases as desorption time increases. Improvements in product purity by CO₂ product purge also depend on the amount of product used for purge [26,35]. Our study [26] found that CO₂ product purity increased almost linearly from 94.3 to 98.5% when the CO₂ purge percentage increased from 0 to 50% (Figure 5 right).

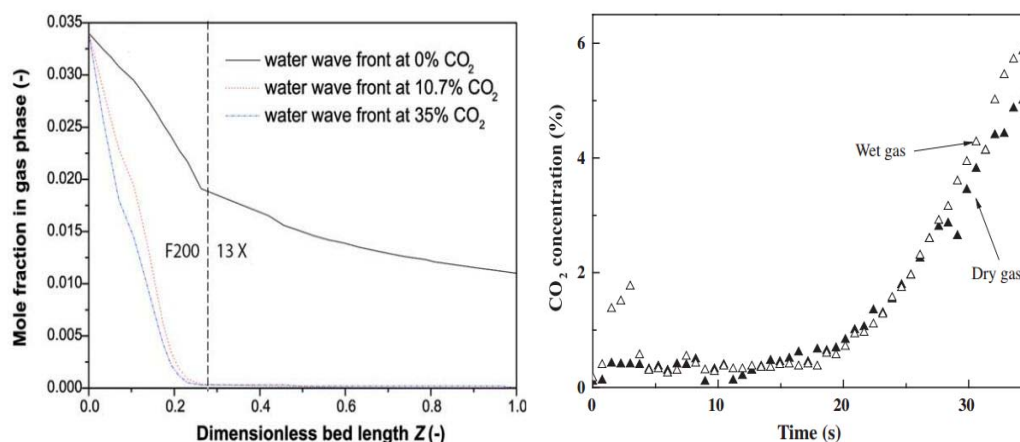


Figure 7: Water and CO₂ concentration in double layered adsorption bed (left) [49] and CO₂ concentration in emission gas using activated carbon as adsorbent (right) [32].

Re-pressurization also affects the process performance. The source of the re-pressurization gas can be either the feed gas or the exhausted gas (CO₂-lean gas). Re-pressurization using CO₂-lean gas can improve CO₂ product recovery [35]. Because the CO₂-lean gas can push the CO₂ front downward to clean the top of the bed, less CO₂ is emitted from the bed during the next adsorption step. However, the effect of re-pressurization is diminished for multiple-bed VSA systems. After several pressure equalizations between the beds, less gas is required for re-pressurization because of the small gap in pressures after equalization and adsorption steps.

CO₂ Capture from Different Sources (Different Inlet CO₂ Concentrations)

A typical flue gas from a fossil fuel power plant contains CO₂ of 10-15% and this emission represents about 50% of all greenhouse gas emissions [41]. With a well-designed VSA process and a good adsorbent such as zeolite 13X, a high CO₂ purity at a high recovery rate can be obtained from flue gases for CCS applications [22,37]. However, a much deeper vacuum pressure ≤ 5 kPa (with higher power consumption), or a two-stage VSA process (which also lead to additional equipment cost) would be needed in order to reach such high CO₂ product purity and recovery [6,14]. Apart from CO₂ emissions from fossil fuel power plants, there are also emissions from other industrial sources where CO₂ concentrations vary over a large range: 15-33% from cement industries, 20-30% from iron and steel industries [42]. The VSA process will show better results when employed to capture CO₂ from these sources. CO₂ product recovery increases at the same vacuum pressure as CO₂ concentration in the feed gas increases (Figure 6 left) [43]. Deep vacuum pressure during desorption steps in CO₂ VSA processes may be avoided when dealing with the gas feeds with higher CO₂ concentrations because of their higher working capacities. Thus, capture cost will decrease as CO₂ concentration in feed gas increases (Figure 6 right) [22].

Effects of Impurities on the CO₂ VSA Process Performance

Water vapor, SO_x and NO_x are common impurities in flue gases from power plants, and these negatively affect CO₂ adsorption capability on zeolites [44,45]. Thus, capturing CO₂ from flue gas at

coal-fired power stations by pressure/vacuum swing adsorption may be complicated by the existence of these impurities when commercial CO₂ selective adsorbents are used. Conventional process designs rely on using a pre-treatment process to remove water, SO_x and NO_x, which adds considerably to the overall cost.

A wash tower is used to reduce the concentration levels of SO_x and NO_x in our CO₂ capture demonstration plant [46]. The trace amounts still remaining may not significantly affect the CO₂ capture process [47,48]. This leaves water vapour as the main impurity and therefore, the discussion on this section focuses on CO₂ capture in the presence of water vapour. Flue gas streams usually contain 8-10% water vapour.

In study conducted in our research group [49], a multiple adsorbent layered column was designed to remove water and CO₂ at the same time from the feed gas. The first layer can be a water reversible adsorbent such as sorbead or activated alumina. This protects the main layer-13X from the negative effects of water vapour on its performance [47,49-51]. Higher CO₂ concentration can also help remove water by internal purge during vacuum desorption (Figure 7 left). As discussed above, activated carbon shows good performance in the presence of water vapour [32]. We found that the effect of water vapour on CO₂ adsorption is not significant on activated carbon, and CO₂ can accumulate at the bottom of bed due to its high adsorption. However, more energy is required to remove water from the bed. Figure 7 right shows CO₂ concentration in the bed outlet gas during the adsorption step for dry gas and wet gas containing 4.6% water.

Power Consumption

Power consumption in PSA/VSA is often calculated according to adiabatic power law [26].

$$PowerCom(\mathbb{I}) = \sum_{i=1}^{i=n} \frac{k}{k-1} \frac{Q_{feed} P_{feed}}{\eta} \left[\left(\frac{P_{feed}}{P_{atm}} \right)^{\frac{k-1}{k}} - 1 \right] \Delta t + \sum_{i=1}^{i=n} \frac{k}{k-1} \frac{Q_{vac} P_{vac}}{\eta} \left[\left(\frac{P_{atm}}{P_{vac}} \right)^{\frac{k-1}{k}} - 1 \right] \Delta t \quad (4)$$

where Q_{vac} is an instantaneous flow-rate (m³/s) and Δt is time interval (s); η (pump coefficient) equals 0.7 and k (specific heat ratio) is 1.28 for CO₂ and 1.4 for air, Q_{feed} represents an instantaneous flue gas flow rate (m³/s), P_{atm} (atmospheric pressure 101.325 kPa), P_{feed} and P_{vac} (kPa) represent instantaneous pressures during adsorption

Table 1: Purity, recovery and specific power consumption of some VSA studies for CO₂ capture.

Process type	Purity, %CO ₂	Recovery, %CO ₂	Sp. power, MJ/kg CO ₂	Reference
VPSA	90	85	1.674	[52]
VPSA	85	79	2.37[exp]	[53]
VPSA	85	79	0.535[sim]	[53]
2- stage VPSA	96	91	0.6444	[14]
2- stage VPSA	95.3	74.4	0.7236	[54]
VSA	93	90	0.432	[55]
Duplex PSA	97.5		0.746	[56]
VSA	90 -95	60 - 70	0.518-0.864	[22]
2-stage VPSA			2.455	[57]
2-stage VPSA	96.54	93.35	0.528	[58]

(feeding) and desorption (vacuum) stages of the process. In this equation, the vacuum power is made up of two parts: power due to desorption and power due to the product purge step (to keep the bed pressure equal to that in the last step).

Most power in VSA process is consumed by vacuum pumps during desorption. The value increases with deeper vacuum desorption. However, CO₂ productivity also increases with deeper vacuum levels. Thus, there is an optimum value of power consumption in the VSA process [26,35]. Measured power consumption is much higher than calculated or simulated values. It is found that the measured power consumption of VSA processing corresponded to theoretical values based on 30% pump efficiency, whereas 70% is often assumed in calculations [37]. From single stage CO₂VSA, deep vacuum is conducted in order to obtain CO₂ product purity of 95%. It must be noted that pump efficiency, η , may decrease with deeper vacuum level because volumetric velocity decreases nonlinearly as deeper vacuum levels are required. When the system is operated at moderate vacuum pressure, the error between experimental result and calculation value may be less.

There are no operating large scale commercial CO₂ capture processes by adsorption technology so far. Published estimates for CO₂ capture power vary widely, mainly as a result of different assumptions regarding technical factors related to plant design and operation. We show some of the published energy consumption of CO₂VSA processes in Table 1.

Conclusions and Future Development

CO₂ product of high purity can be obtained from fossil fuel flue gas streams, at high recovery rates using VSA cycles; however, very low vacuum pressure levels are required during the desorption step. Two-stage VSA processes can be used, which may avoid operating at deeper vacuum with each unit operating at moderate vacuum pressure. However, capital cost will increase because of the extra VSA unit. TVSA may be promising (VSA with slight increase in bed temperature during desorption) since it combines the merits of rapid vacuum swing and effects of temperature rise on the adsorption equilibrium. In this case, the system will not need to operate at deep vacuum. High performance may be generally achieved at intermediate vacuum levels as CO₂ concentration in feed gas streams increases. Therefore, VSA technology is very promising for CO₂ capture from

CO₂ sources where the inlet CO₂ concentrations are higher such as in cement, iron and steel, etc. manufacturing.

Both multiple-layered adsorption beds and adsorbents with hydrophobic characteristics can be applied for eliminating the negative impact of impurities, such as water vapour, traced SO_x and NO_x, on CO₂ capture performance, but more energy may be consumed for removing the collected impurity from the system. Therefore, new adsorbents, which have higher CO₂ working capacity, high selectivity, and the characteristics of easy desorption and high tolerance for impurities are still required.

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