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Adsorption technology for CO_2 separation and capture: a perspective

Paul A. Webley

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Abstract The capture of CO_2 from process and flue gas streams and subsequent sequestration was first proposed as a greenhouse gas mitigation option in the 1990s. This proposal spawned a series of laboratory and field tests in CO_2 capture which has now grown into a major world-wide research effort encompassing a myriad of capture technologies and ingenious flow sheets integrating power production and carbon capture. Simultaneously, the explosive growth in materials science in the last two decades has produced a wealth of new materials and knowledge providing us with new avenues to explore to fine tune CO_2 adsorption and selectivity. Laboratory and field studies over the last decade have explored the synergy of process and materials to produce numerous CO_2 capture technologies and materials based on cyclic adsorption processes. In this brief perspective, we look at some of these developments and comment on the application and limitations of adsorption process to CO_2 capture. We identify major engineering obstacles to overcome as well as potential breakthroughs necessary to achieve commercialization of adsorption processes for CO_2 capture. Our perspective is primarily restricted to post-combustion flue gas capture and CO_2 capture from natural gas.

Keywords CO_2 capture · Adsorption processes · CO_2 adsorbents · Pressure swing adsorption · Temperature swing adsorption

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P. A. Webley (✉)
Department of Chemical and Biomolecular Engineering, Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), The University of Melbourne, Parkville, VIC 3010, Australia
e-mail: paul.webley@unimelb.edu.au

1 Introduction

Over the last two decades, the management of CO_2 has become a major research "industry". Carbon dioxide is one of the most ubiquitous molecules under investigation in global university and industrial R&D efforts. In particular, the idea of separating CO_2 from process gas streams on a large scale with the goal of either using or storing the purified form has evolved from desktop studies and small scale contributions in the 1990s to major international efforts at pilot and demonstration scale today. Scrubbing CO_2 from process gases with liquid solvents such as methyl ethylamine (MEA) and related solvents has been the benchmark technology for over 60 years and is still the reference to which alternative technology should be compared (Wang et al. 2011). The urgency of climate change however, has spawned a concerted global effort to consider other, potential lower cost capture technologies. Amongst these alternative technologies are adsorption based CO_2 capture, membrane processes, cryogenic methods, hydrate processes, electrochemical techniques as well as other niche methods (Markewitz et al. 2012). These alternate technologies are being adapted and developed for CO_2 capture for such diverse applications as post combustion flue gas, pre-combustion process gas such as that found in the integrated gasification combined cycle (IGCC) process or other gasification processes, natural and biogas systems, cement and steel making applications, and the food and beverage industry.

The use of adsorption technology to separate CO_2 from gas streams is not new. Early applications in the 1950s relied on molecular sieves, alumina and silica materials for removing trace CO_2 from air in enclosed environments such as submarines (Colburn and Dodge 1951). One of the first reports of cyclic adsorption processes for recovering

CO_2 at high purity from process streams (natural gas) containing bulk quantities of CO_2 is that of Collins (1973). However, the use of adsorption processes for recovering CO_2 at high purity from flue gas streams containing bulk quantities of CO_2 has been explored only comparatively recently starting with the investigations of Takeguchi in the early 1990s (Takeguchi et al. 1993). To date, there have been occasional pilot scale demonstration plants but no commercial examples of adsorption processes for CO2 capture from low pressure flue gas streams (Ishibashi et al. 1996; Sjostrom et al. 2011; Rao et al. 2012; Qader et al. 2009; Liu et al. 2012b). Opinions offered in this perspective will address this rather pessimistic finding with a view to identifying key challenges to overcome before commercial exploitation can be envisaged.

Early process work on developing pressure and temperature swing systems relied on existing adsorbent materials from the zeolite, alumina, silica gel, and carbon families. The 1980s and 1990s saw rapid development of novel molecular sieves in the silica-aluminate, ALPO, SAPO and mesoporous zeolite families (Murakami et al. 1986). Within the last two decades, there has been an explosion of materials science research with the arrival of metal organic frameworks, nanostructured carbon and inorganic (oxide) materials and development of hybrid organic–inorganic materials with either tethered or occluded organic moieties within the inorganic substrates (Choi et al. 2009). In parallel with the development of these synthetic techniques has been the simultaneous advance in characterisation techniques which has facilitated understanding and engineering of new materials at ever smaller scales and with enhanced precision. Seldom does a week pass without the announcement in the literature (and popular scientific press) of new materials advocated for CO_2 capture. While the number of new adsorbent materials reported has proliferated, only a very select few will undergo bench-top testing and even fewer pilot testing in part due to limited availability of materials (many exotic adsorbents are made at less than 1 g level) but also due to practical constraints placed on materials (such as operation in humid environments) which are often not the goal of initial materials research.

Our goal in this perspective is not to review the literature in the field but rather to discuss the issues confronting researchers new to the field or adsorption based CO_2 capture. This perspective is arranged as follows. The application arena of CO_2 capture by adsorption is first classified since the requirements on the adsorbent and process vary widely from one field to the next. Then each application area is discussed with targets and engineering constraints identified. Finally, we summarize the current status and indicate future research and development needs for adsorption based CO_2 capture.

2 Application space for adsorption-based CO_2 capture

The applications and process streams which require removal and recovery of CO_2 include: post combustion flue gases arising from fossil fuel oxidation; synthesis gas (CO_2, H_2, CO_2, H_2O) such as those arising from hydrogen production from natural gas, IGCC processes, off gas from direct reduction of iron; conventional and unconventional natural gas, biogas, vent streams in the food and beverage industry, and vent streams from cement manufacture. We confine our attention in this perspective to the areas of post combustion flue gas and CO_2 capture from natural gas sources since these application areas have dominated the literature over the last decade.

2.1 Post combustion flue gas capture with the goal of sequestration

Recovering CO_2 from large scale post combustion flue gas streams such as those arising from coal-fired power plants is extremely challenging, if the goal is to mitigate climate change. Given the large specific CO_2 emission of a coal fired power plant (generally about 800 kg CO_2/MWh), a 500 MW coal fired power plant will emit on the order of 10,000 tonnes of CO_2 per day in a flue gas stream of 10–15 % CO_2 saturated with water at atmospheric pressure. The only gas separation technologies on this scale with an industrial experience base are cryogenic technologies and even here the scale has not yet reached these limits. Unfortunately, cryogenic processes are not an attractive option for CO_2 capture from post combustion flue gas streams since compression of the flue gas containing only 15 % CO_2 to pressures required for CO_2 liquefaction is not practical, not to mention the need to pre-dry the flue gas stream.

The current preferred option for CO_2 capture from coal-fired post combustion flue gas is scrubbing with chemical liquid solvents (Rubin et al. 2012). In this process, a solvent (often MEA) in aqueous solution is reacted with CO_2. The liquid is conveyed to a separate column for regeneration. The process has the advantage of integration with the power plant in which steam from the low pressure turbine is used for regeneration of the solvent and recovery of the CO_2. High purity CO_2 (>99 % purity) is produced at high CO_2 recoveries (>90 %). The technology is mature although the recent focus on carbon capture has led to rapid and recent improvements in this technology. The energy of regeneration has been reported from 2 to 4 MJ/kg CO_2 (strongly dependent on solvent type and process conditions) with a corresponding power plant energy penalty of 25–35 % or 7–10 percentage points, depending on the base load efficiency of the power plant in the absence of carbon capture (Bhown and Freeman 2011). The largest units in progress at the time of writing are at a 110 MW scale (SaskPower 2013) and significant additional work is needed to scale the technology to 500 MW and beyond. Nevertheless, this technology represents the benchmark to which adsorption processes must be compared.

A large portion (20–40 %) of the regeneration energy used in the liquid scrubbing process is used to heat and evaporate water in the stripper (Oexmann et al. 2012). In principle, an adsorption process can avoid the evaporation component thereby offering potentially lower energy requirement. However, if adsorption based systems are to be competitive, they must at least match if not improve upon both the overall energy and capital costs of liquid scrubbing systems.

Adsorption based CO_2 capture from post combustion flue gas can be classified based on the mode chosen to regenerate the adsorbent: either an increase in temperature (temperature swing adsorption) or a reduction in pressure (pressure or vacuum swing adsorption). Both cases place differing demands and constraints on the adsorbent and the process and are discussed separately below.

In addition to capture from coal fired power plants, the application of adsorbents to capture CO_2 from natural gas fired combined cycle plants have also been studied. (Grande et al. 2009; Zhao et al. 2013b). In this case the concentration of CO_2 in the flue gas is 3–6 % although the volume flows may be considerably smaller than in the case of coal-fired power plants.

2.1.1 *Temperature swing adsorption processes (TSA)*

TSA adsorption processes for CO_2 capture have been investigated by numerous groups using dry regenerable sorbents in a circulating fluidised bed arrangement (Zhao et al. 2013b), amine loaded sorbents (Sjostrom et al. 2011), zeolites in fixed beds with indirect heating (Tlili et al. 2009) and even electrical heating systems (Grande and Rodrigues 2007a). Adsorbents for temperature swing processes applied to post combustion flue gas must respond strongly to changes in temperature ideally in the range 30–150 °C. This is the range of temperature at which heat is available at the power plant (e.g. low pressure turbine, flue gas waste heat, CO_2 compression after cooler heat, etc.) and can be used to contact the adsorbent either directly or indirectly. As a result, chemisorbents with heats of adsorption in the range 40–70 kJ/mol CO_2 are suitable. These are characteristic of amine and imide hybrid materials which have been extensively studied over the last 10 years (Zhao et al. 2013a). Although physisorbents may also function in this range (see application of 13X zeolite to high temperature capture (Xiao et al. 2012)), their CO_2 working capacity is diminished and fast cycling is required to offset the lower working capacity. In addition to the need for acceptable CO_2 working capacity, chemisorbents for TSA application must also be tolerant to water and impurities such as SO_X, NO_X and even occasionally HCl which may be present in the flue gas and should preferably not adsorb nitrogen. This last requirement is frequently met with most chemisorbents. If water is strongly adsorbed (and in the case of dry regenerable adsorbents is needed), the touted advantages of adsorbents over liquid absorbents disappear since energy must be expended in desorbing water. We encourage workers who are developing new chemisorbents to study the simultaneous adsorption and desorption of water in their work.

The largest drawback of the thermal swing adsorption cycles are the large cycle times needed if the gas–solid contacting devices are restricted to fixed beds. Heating and cooling times (by hot or cold gases) in conventional packed beds of pellets are of the order of hours—this effectively restricts these TSA systems to small scale applications. Alternative adsorbent structures and processes are essential if TSA is to find an application in large scale CO_2 capture. Circulating fluidised beds or moving beds are logical solutions to this problem essentially mimicking the liquid absorption systems. Unfortunately, circulating fluidised beds frequently rely on the flue gas stream to simultaneously elevate the dry adsorbent leading to a co-current contacting profile and therefore lower capacity than counter current systems. While mechanically difficult to operate, these processes do have precedence at large scale e.g. fluidised bed catalytic crackers, but it is difficult to see how the capital cost of a circulating fluidised bed system can be competitive with conventional liquid scrubbing in packed towers. Attrition of the adsorbents is a significant issue as well as poisoning of the adsorbents by impurities such as SOx and NOx. An alternative to moving or circulating beds are rapid thermal swing processes in fixed contactors such as those under development in the Koros Group (Lively et al. 2009). This is an extremely promising approach and is arguably the leading contender for “intensifying” TSA processes. Instead of cycle times of hours, cycle times of minutes are necessary if we are to see large scale deployment of TSA systems in CO2 capture from power plants.

2.1.2 *Pressure swing adsorption processes*

Pressure swing processes have the advantage over TSA in that rapid cycling (minutes or even seconds) is possible in fixed beds leading to much smaller bed sizes. Compression of post combustion flue gas beyond approximately 1.5 bar is not cost effective though, given the large content of nitrogen and the low flue gas pressure. For this reason, vacuum swing adsorption (VSA) is the preferred mode of operation for post combustion flue gas. A large number of studies by many groups have examined the performance of a range of adsorbents and process cycles employing VSA as the regeneration mode (Xu et al. 2013; Wang et al. 2013; Haghpanah et al. 2013; Ebner and Ritter 2009). Adsorbents for VSA based on physisorption are more appropriate—the most common adsorbents employed are 13X zeolite (ΔH ~45 kJ/mole) and activated carbon (ΔH ~15–30 kJ/mole). Our earlier analysis (Maring and Webley 2013) has showed than an ideal heat of adsorption in the range 35–45 kJ/mol provides an appropriate compromise between higher CO_2 working capacity and lower regeneration energy. Adsorbent selectivity (CO_2 over N_2) and thermal effects have a more significant effect on the specific power consumption than does CO_2 adsorption capacity. Although many groups have reported promising CO_2 capacity on very high surface area metal organic frameworks, continual increase in surface area is not necessarily beneficial to overall performance, becoming more detrimental as the heat of adsorption of N_2 increases (Maring and Webley 2013). Adsorbent development for VSA applications should therefore focus on reducing the nitrogen adsorption amount and reducing the temperature swing accompanying adsorption of CO_2.

Impurities and water present in flue gas pose a significant challenge to VSA processes for CO_2 capture since physisorbents are generally used. Most adsorbents which are selective for CO_2 will adsorb water and other acid gases in preference to CO_2 reducing the CO_2 capacity. We have shown that this problem can be ameliorated by layering the bed (Li et al. 2011) with little impact on CO_2 purity and recovery provide appropriate process cycles and process conditions are imposed. However, the desorption of water in the cycle presents an added energy penalty and is less desirable than adsorbents which excludes water entirely. Upstream dehydration of the flue gas is not a practical option at the scale of power plant post combustion flue gas.

Research groups including our own have reported that CO_2 purities in excess of 90 % are achievable with recoveries ranging from 70 to 90 %. In all cases, however, deep vacuum levels (2–10 kPa) are needed to achieve these recoveries and purities and it is important to discuss this issue since it provides guidance for workers who are interested in developing improved adsorbents. Single stage vacuum blowers used in VSA industry are capable of providing vacuum levels down to approximately 25 kPa (absolute). Deeper vacuum (<5 kPa) requires multistage units adding to cost and power requirements. In addition, any pressure drop between the bed and the vacuum pump is detrimental to performance and minimizing the pressure drop results in very large suction and valve line sizes. This is a significant limitation and raising this vacuum level to 20–30 kPa should be a focus of future R&D efforts. Both the shape of the adsorption isotherm as well as the process cycle can influence this required pressure level. Furthermore, operating valves and beds against low vacuum levels (3–10 kPa) is costly especially if rapid cycling is envisaged.

The power required to desorb CO_2 from the physisorbents under vacuum has been reported by many workers and ranges from 0.6 to 6 MJ/kg CO_2 (Liu et al. 2012b). The lower end of this range is significantly lower than that for liquid scrubbing (which ranges from 2 to 4 MJ/kg), but it is important to note that the VSA process uses electrical energy. Using a 30 % Carnot factor, a VSA energy use of 1 MJ/kg equates to a thermal load of 3.3 MJ/kg which is comparable to but not significantly better than existing liquid solvent systems. Researchers should carefully analyse their proposed adsorbents for the total energy usage by process simulation or at least simple indicative models.

Finally, it is worth noting the limitations of the VSA process with regard to scalability. The largest vacuum trains commercially available are capable of providing approximately 100,000 m3/h at 50 kPa vacuum. This equates to capturing CO_2 from a 50 MW power plant assuming a vacuum level of 50 kPa can produce CO_2 at a purity of 95 %. A 500 MW power plant will require ten parallel trains of these vacuum blowers. Of course, bespoke high volume vacuum machinery can be developed but the limitation will be to ensure that high purity CO_2 gas is produced at shallow vacuum levels (e.g. 50 kPa).

In summary, research in VSA systems should focus on

- Adsorbents with high CO_2/N_2 selectivity, tolerance to water (with negligible adsorption of water), and tolerance to acid gases
- Processes and adsorbents which allow the vacuum pressure to be raised to 20–30 kPa while still producing gas purity of 95 %

2.2 CO_2 capture from natural gas streams

Natural gas streams derive from a large variety of sources including conventional, unconventional, and biogas. Conventional sources are typically available at high pressures (50–100 bar) and may contain variable amounts of CO_2 ranging from a few percent to greater than 10 %. Removal of trace CO_2 and sour gases such as H_2S from these sources is well established technology in the natural gas industry employing liquid scrubbing technology for sweetening the gas followed by molecular sieve dehydration in preparation for the liquefaction train. Wells containing high levels of CO_2 (>10 %) are now of increasing interest and presents an opportunity for adsorptive processes. On the other hand, unconventional sources of natural gas such as coal seam gas or shale gas may be available at much lower pressures and can have highly variable levels of CO_2. These natural gas streams are usually saturated with water and may contain significant levels of H_2S as well as higher hydrocarbons. This presents additional challenges to the researcher.

2.2.1 *Conventional natural gas*

Capture of "bulk" CO_2 (>10 %) from conventional natural gas streams by adsorption processes presents unusual and severe challenges to the adsorbent developer but also opportunities. The primary goal in this application is to produce purified natural gas so loss of the methane (and higher hydrocarbons) is to be avoided at all costs. Since the total stream pressure can be 70–100 bar, pressure swing processes are attractive provided the CO_2 can be recovered without needing to extend the pressure range down to vacuum levels. Adsorbents which show good adsorption capacity upto high pressures (such as high surface area metal organic frameworks) may have a role to play in this regard. Unfortunately, unless the CO_2:CH_4 selectivity is very large, co-adsorption of CH_4 during the adsorption step and subsequent loss during the CO_2 recovery step will lead to unacceptable economics.

A desirable adsorbent should therefore completely exclude methane from the internal structure of the adsorbent while permitting rapid access of CO_2 and high CO_2 capacity. This rules out large pore adsorbents such as 13X zeolite. Small pore materials are more suitable. Zeolites 3A and 4A, DDR, and SAPO-34 as well as "trapdoor" chabazite zeolites we have recently developed (Shang et al. 2012) show virtually exclusive access of the adsorbent to CO_2 regardless of operating pressure. However, such a delicate sieving mechanism results in kinetic limitations for the CO_2 which should be the target of future research in these materials. These adsorbents are also sensitive to the presence of moisture in the flue gas stream and must be protected. Impurities in the gas such as H_2S present primary challenges to application of adsorption to CO_2 capture from natural gas. In addition, higher hydrocarbons are valuable constituents of the natural gas and should not be taken up by the adsorbent. This combination of unusual constraints placed on the adsorbent indicate that considerable development is required both of adsorbents and process cycles before we will see emergence of adsorption process in the natural gas industry beyond current dehydration service. However, the advent of molecular pore engineering synthesis and characterisation techniques for both metal organic frameworks as well as zeolite structures is likely to be a very useful tool for developing the required adsorbents.

2.2.2 *Biogas and landfill gas*

Biogas and landfill gas present very promising opportunities for adsorption based CO_2 capture because of the low pressures of these streams, the relatively high CO_2 content, and the low flow rates. In general, the naturally occurring sources of these gases (landfills, bio-digesters, etc.) result in a biogas stream at atmospheric pressure with upto 60 % CO_2 and a variety of commercial units have been demonstrated for the enrichment of these streams using adsorption processes (Grande and Rodrigues 2007b). In most cases, VSA is employed but frequently upstream removal of H_2S and dehydration is needed (using a front-end TSA unit) to ensure robust operation of the VSA system. The high selectivity of CO_2 over CH_4 for most adsorbents means that large pore adsorbents are suitable and very high purities of both CO_2 and CH_4 are attainable if appropriate process cycles are implemented (Spoorthi et al. 2010). Challenges for the researcher include the handling of high levels of H_2S and water, and the need for low energy requirements.

2.3 Emerging application areas for adsorption based CO_2 capture

The application areas discussed above in the context of CO_2 capture are the ones which have attracted the most attention in adsorbent development studies. However, there are other opportunities which in some respects are more suited to adsorption processes. Amongst these are recovery and reuse of CO_2 from the vent streams of beverage bottling plants, removal of CO_2 from H_2PSA tail gas in reformers or direct iron reduction gas streams (Voss 2005; Haraoka et al. 2013), recovery of CO_2 from cement manufacturing (Bosoaga et al. 2009), capture of CO_2 from IGCC process gas streams (Casas et al. 2013; Beaver and Sircar 2010) and high temperature capture of CO_2 from combustion processes using calcium oxide materials (Liu et al. 2012a). All of these applications benefit from higher concentrations of CO_2 and, in many cases, the goal is to remove CO_2 from the more valuable product (e.g. H_2 in the syngas process) rather than recover the CO_2 at high purity. The demands placed on the adsorbents for the high temperature applications are similar to those discussed earlier (tolerance to impurities, water etc.) but in addition, the high temperature service can lead to sintering of many oxide adsorbents and resulting decline in performance. In many cases (e.g. calcium looping), morphological changes to the adsorbent leads to volume change and dusting or attrition of the adsorbents. Combining adsorptive removal of CO_2 with chemical reactions represents yet another example in which the advantages of adsorption processes are exploited in driving chemical reaction equilibrium to a desirable conversion. In this context sorption enhanced water gas shift reactors are a promising example (van Selow et al. 2009; Wright et al. 2009). These research fields are still nascent and present exciting opportunities for new researchers entering the CO_2 capture field.

As an example of a niche opportunity for exploiting the advantages of adsorption processes for CO_2 capture, we have recently demonstrated a VSA system for enriching CO_2 from the vent line of a bottling line in a beverage plant. Liquid scrubbing systems using chemical solvents are not suitable for this application given the end use of the CO_2 product (consumable beverages). In this application, a gas vent stream containing ~70 % CO_2 is sent to a three bed VSA system using 13X zeolite operating between 100 and 20 kPa to recover more than 80 % of the gas producing a CO_2 stream of >96 % purity suitable for recycle to the CO_2 feed to the beverage plant. The relatively low water level in the feed stream (saturated with water at 15 °C) was readily accommodated by the 13X zeolite system.

3 Conclusions and suggestion for future development

To date there are no operating large scale commercial CO_2 capture processes based on adsorption technology. In this perspective we have put forward the rationale for this position. For post combustion flue gas capture using VSA, the scale of adsorption processes is limited to about a 50 MW flue gas stream using todays largest vacuum pump machinery unless parallel trains are used or custom built machinery is used for larger scale operation. Developing adsorbents and cycles which permit higher vacuum levels to be used while retaining the high purity will extend the size of these systems. Temperature swing processes for post combustion flue gas are limited due to large bed sizes for fixed bed operation—practical operation will require dramatic reduction in cycle time such as rapid swing TSA processes or moving/circulating systems. Combinations of these two options (VSA and TSA) are also promising since they may combine the merits of rapid vacuum swing processes without the need for deep vacuum.

Adsorbent development for both vacuum and temperature swing processes must address the issue of water adsorption as well as handle impurities such as NO_X, SO_X. Attention should be focused on reducing nitrogen adsorption and, in the case of physisorbents, mitigating the temperature swing accompanying the pressure swing.

In the application of adsorption to capture of CO_2 from natural gas streams, there is great scope for sophisticated adsorbent development which must meet the goals of exclusive CO_2 capture at high pressure with minimal losses of methane and higher hydrocarbons. In the context of CO_2 capture from biogas, the major drawbacks are the sensitivity of the materials to H2S and water. Development of H2S tolerant materials will provide a major boost to the extension of adsorption technology into the natural and biogas areas.

Finally, there are additional opportunities for CO_2 capture at a scale and set of process conditions very suitable for adsorption processes. These include streams emanating from cement, iron and steel, pre-combustion, and food and beverage applications, to mention a few. These applications all differ in their demands on the adsorbent and process but the immaturity of adsorption processes suggest that rapid inroads can be made using adsorption processes.

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