Carbon Capture Storage Review

Surface Measurement Systems

Surface Measurement Systems
World Leader in Sorption Science

Contents

Introduction

Efforts to address global warming and its associated challenges have been ongoing for several decades. Historically, before the industrial revolution, the atmospheric CO_2 concentration was around 280 ppm.[1] In 2022 the global average atmospheric CO_2 was 417 ppm.[2] While there is no specific ppm target for combating climate change, efforts are focused on reducing and stabilising CO_2 concentrations to avoid severe consequences of global warming.

In 1988 the United Nations Environment Programme (UNEP) and the World Meteorological Organisation (WMO) established the Intergovernmental Panel on Climate Change IPCC which has dedicated its recourses to assess the scientific evidence on climate change, its impact, potential mitigation, and adaptation pathways.[3] The IPCC played a significant role in shaping the Paris Agreement through scientific assessments. In COP21 long term goals and targets were set to establish a framework for international cooperations to reduce global warming below 2 °C and pursue efforts to limit the temperature increase to 1.5 °C.[4]

The Paris Agreement aims to achieve a balance between anthropogenic emissions of greenhouse gases, with the goal of reaching net-zero emissions in the second half of the century.[2] There are various CO_2 reduction schemes and technologies that aim to mitigate emissions and combat climate change. One of the direct approaches involve transitioning to renewable energy by using sources such as solar, wind, hydroelectric, and geothermal power can significantly reduce CO_2 emissions. However, the energy transition must be accompanied by technologies which mitigate existing emission sources, or reverse existing atmospheric release. Carbon Capture Utilisation and Storage (CCUS) are approaches in the field of CO_2 mitigation involved capturing emissions where the fate of captured CO_2 have different routes and destinations.

The primary objective of carbon capture storage (CCS) is to capture CO_2 emissions and permanently store them underground, preventing their release into the atmosphere. As of September 2022, there have been 196 projects in the CCS facilities pipeline with 61 new CCS facilities added in 2022 alone.[5] Globally there are 30 CCS facilities in operation currently with the capacity to capture and store around 43 million tonnes of CO_2.[5]

The upfront investment and cost of implementation required for CCUS infrastructure, including capture, transport, and storage, can be a significant barrier to its widespread deployment. Governments and international organisations have recognised the importance of CCS in achieving climate goals and have implemented policies and incentives to support its development. A great deal of technological progress is similarly

required to be able to close the CO_2 lifecycle. In a first instance, selectively targeting and concentrating CO_2 in the wide range of conditions from emission sources or the atmosphere. This must be followed by the infrastructure to transport it where it will upconverted into usable products – or will be stored deep underground. The latter processes also require a step change in material science for the development of novel catalytic materials for up conversion, and a fundamental understanding of CO_2 binding in solid materials such as building materials or reservoir rocks.

Sorbents – porous media, polymers, or finely divided powders, are materials that can be relevant at each stage of the CCUS pipeline. They can act as selective uptake materials for CO_2 at the capture stage, they can be used as storage media for solid state transport, or through reactions act as permanent sinks, or catalyse various reactions. They are a key developing technology stack, with multiple global research initiatives pertaining to their discovery, optimisation and scale up for use in various CCUS application.

This white paper outlines the required advances in sorbents with relevance to CCUS technologies and addresses the challenges associated with accurately evaluating successful materials for carbon capture. Surface Measurement Systems (SMS) provides a suite of characterisation instruments tailored to solving real world carbon capture problems focusing on the evaluation on advanced materials used in CCUS.

CCUS – conditions and challenges

Capture

Carbon capture technologies can be used to approach target emissions at different stages of CO_2 emissions. We can classify technologies broadly as being targeted at point sources – capture of CO_2 before it is being released into the atmosphere, or Direct Air Capture (DAC) of already emitted CO_2 in the atmosphere.

Point source technologies can then broadly be ranked as a function of their impact. Generally, the sources with the highest and most concentrated CO_2 emissions make first candidates for carbon capture targets. The lowest hanging fruit in terms of contributions and global impact can be found in flue gas streams resulting from fossil fuel burning and raw material manufacturing like steel and cement. Some of the main sources of point source technologies target pre-combustion capture, post combustion capture and oxyfuel combustion capture. A schematic of these technologies is illustrated in Figure 1. Identifying the differences between temperatures and pressures associated with these techniques, and understanding the roles they play in the capture and storage process is

essential when attempting to evaluate the capture efficiency of sorbent material active in carbon capture techniques. Current research in the field eludes to a gap which exists between the conditions under which these technologies are studied and their real world application conditions. Table 1 summaries the different conditions associated with different capture methods.
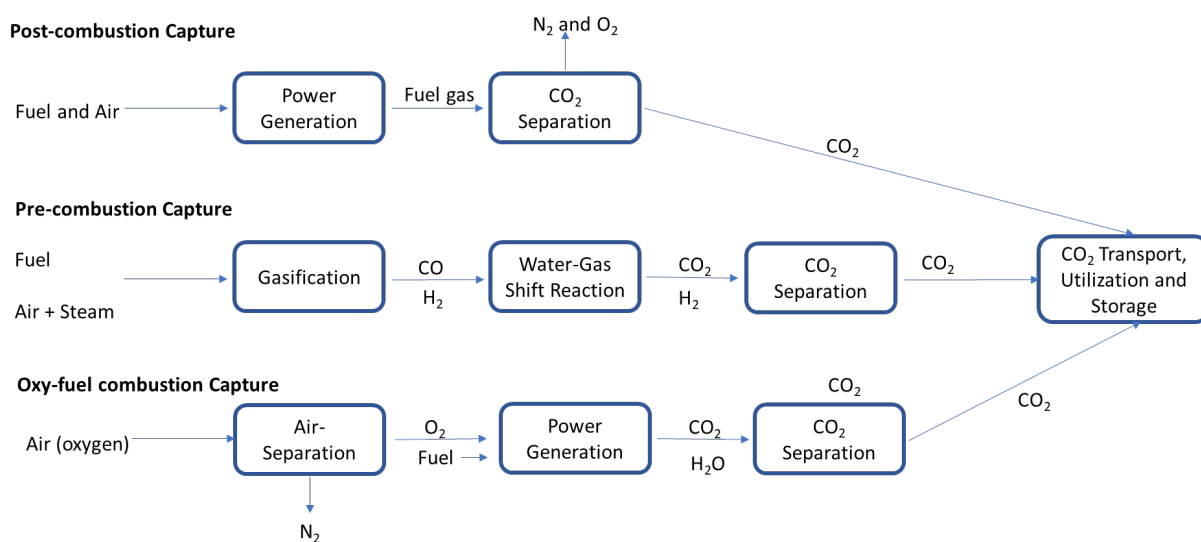

Figure 1. Schematic flow diagram of post-combustion, pre-combustion and oxy-fuel combustion carbon capture technologies.

Table 1. Table highlighting different capture methods and the temperatures and pressures required for both capture and storage methods.

Capture Method	Capture		Storage	
	Temperature (°C)	Pressure	Temperature (°C)	Pressure
Post Combustion	45-125	atmospheric	30-50	atmospheric
Pre-Combustion	250-500	20-40 bar	< 40	150 bar
Oxy-fuel	650-950	200 bar	30-50	100-110 bar
DAC	-20-40	atmospheric	10-40	atmospheric

Post Combustion Capture

In post combustion carbon CO_2 is removed from flue gas streams – resulting from the combustion of fossil fuels like coal or natural gas. Flue gas streams are typically around 15% by volume and possess up to 95% relative humidity at atmospheric pressures and high temperatures between 47 °C and 127 °C.[6,7,8] It requires energy intensive cooling

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systems which cools the flue gas leaving the combustion site to 30 °C-50 °C.[9] This is the optimal operating temperature for most carbon capture technologies. The challenge lies in ensuring other impurities such as particulates, sulphur dioxide, nitrogen oxides and corrosive substances including chlorine and fluorine, do not interfere with the capture process.[7] In a coal fired power plant, post combustion capture is conceptually the simplest scheme for controlling carbon emissions. Post combustion capture technology can be retrofitted into existing industrial power stations and integrated into new ones.

Pre-Combustion Capture

Pre-combustion carbon capture is a direct strategy involved in removing CO_2 from fuel sources prior to combustion. This process is commonly applied in Integrated Gasification Combined Cycle (IGCC) power plants. In the gasification process, fossil fuels such as coal undergo a pretreatment stage which includes partially oxidizing coal in air and steam under high temperatures (around 1500 °C) and pressures (over 40 bar) to produce synthetic gas or syngas.[10,11] This is a composition of CO, CO_2, H_2, and small amounts of CH_4. The syngas undergoes a water-gas shift reaction to produce additional hydrogen and carbon dioxide. The hydrogen byproduct can be used as a gaseous fuel in fuel cells, and gas turbines.[10] The CO_2 concentration in the mixture can be between 15% and 60% by volume.[12] Sorbent CO_2 removal from syngas occur at temperatures between 250°C-500°C and pressures of 20-40 bar.[13] Operators capture, transport, and sequester the CO_2 in the mix, leaving an H_2-rich fuel for combustion.

Oxy-fuel Combustion

Oxy-fuel combustion involves the combustion of flue gas in the presence of pure oxygen instead of air. This removes the large nitrogen component found in air and as a result produces a flue gas stream with a higher concentration of CO_2 with its water vapour content easily removed via liquid condensation and compression steps.[10] Although pretreatments are still required to remove impurities, this step simplifies the capture process and reduces nitrogen oxide emissions. However, there are challenges associated with the production and distribution of pure oxygen and separation of oxygen and CO_2. Oxy combustion technology can be applied by modifying conventional combustion systems such as gas turbines and boilers. Air separation units are used to separate oxygen from flowing air through membranes feeding oxygen into the combustion systems. Air separation units can produce up to 99% pure oxygen and operate at 30 bar pressure.[14] Activation temperature ranges from 650°C to 950°C. For transportation using pipelines, the CO_2 stream is firstly compressed to overcome frictional and static pressure drops which is typically between 100-110 bar and a temperature above the critical value in the range of 30°C -50°C.[15]

Other Point Source Capture Sources

In addition to the widely recognised consequences of fossil fuel combustion, other industries also play a role in contributing to the rise in CO_2 emissions. The cement industry corresponds to about 6-7% of global anthropogenic emissions, 60% of which comes from the mineral decomposition of $CaCO_3$ to CaO. CO_2 is a byproduct of this chemical conversion used in the production of cement.[16] CCUS plays a prominent role in decarbonising the industry.

CCUS technologies have been also utilised in the iron and steel industry which is a dominant carbon emission source. Carbon capture technologies can be retrofitted into existing steel plants using post-combustion or oxyfuel methods. However, applications are still in its infancy due to multi point source emissions in plants and gaps in knowledge with regards to performance and economic evaluations.[17]

The chemical sector is another industry which produces CO_2 emissions. It underpins manufacturing supply chains by providing chemical materials and products to a range of industries such as aerospace, automotive and pharmaceuticals. The chemicals industry is responsible for releasing 2 $GtCO_2$ per year resulting to about 5% of CO_2 global emissions.[18] The routes for decarbonisation using CCUS involve capture at stages of synthesis and end of life of the product. CO_2 can be captured using DAC methods or via a combination of DAC and point source capture which is more favourable in terms of being cost effective and energy efficient.[16] For example, CO_2 capture in ethanol facilities are integrated at two major source points: during the fermentation process where more than 85% volume of CO_2 is formed as a byproduct, and during fuel burning.[19] The high purity of the fermentation streams are ideal points for CCUS.

Direct Air Capture

Another approach for CO_2 mitigation involves DAC technology which removes dilute concentrations of CO_2 directly from ambient air, currently around ~400 ppm.[20] The process begins with the intake of large volumes of air from the atmosphere which is 350 times less CO_2 concentrated than that found in a conventional coal-based flue gas.[21] Air is directed towards contactor units densely packed with sorbent materials.[13] The temperature at which capture processes occur is dependent on sorbents being used. These sorbents have a high affinity for CO_2 and can interact to facilitate capture. CO_2 is separated from water during integrated condensation steps before undergoing compression for subsequent transportation, storage, and utilisation. This heat intense calcination process draws the most energy. The thermal energy input for sorbent lead DAC processes requires 6 GJ tCO_2^{-1} and electrical requirements have been measured to be about 1.5 GJ tCO_2^{-1}.[22] To reflect real world applications DAC technologies should be

studied within the temperature range of -30°C to 50°C at 400ppm in the presence of humidity to be inclusive of broad geographical conditions.[22]

Transportation

The process of transporting CO_2 within the CCS framework plays a pivotal role in mitigating the adverse effects of CO_2 emissions on the environment. The process involves several essential steps to ensure the secure and efficient movement of CO_2 from its source to designated storage or utilisation sites. Captured CO_2 is typically in gaseous form at relatively low pressure.[23] To make it more manageable for transportation, it must undergo compression. CO_2 is compressed using high pressure compressors with operational capacity of more than 10 Mpa. One of the most common modes of transportation is through pipelines. Similar to natural gas pipelines, regulations must meet specific safety and corrosion resistance standards.[23] For shorter distances transportation may involve tanks or specialised containers that can withstand high pressures. An attractive alternative is the use of sorbent materials within gas cylinders, that can lower the total storage pressure by reversibly adsorbing CO_2.

Utilisation

There is economic scope for creating markets for CO_2-based products, such as fuels, chemicals, building materials, or feedstocks for other industrial processes. Carbon neutral fuel or synthetic fuel aims to offset their carbon footprint. For example, the synthesis of electrofuels utilises CO_2 via the interaction with hydrogen from water electrolysis to produce natural gas or methane.[23] Carbon feedstock can also be used to create chemicals and polymers. Waste products can be used to create carbamates. Dimethyl and ethyl carbonates can be used in applications such as electrolytes in batteries and solvents.[24] The interaction between CO_2 and epoxides creates synthesised polycarbonates which are versatile materials involved in the production of plastics used in optical lenses and consumer goods.[24] Reacting CO_2 with hydrogen can create methanol and with the use of a catalyst, create formic acid which can be used in the formation of dyes, preservatives, and pharmaceuticals.[23] The food industry has also benefited from CCU byproducts by dissolving CO_2 into liquids under controlled conditions forming carbonated beverages that provide the desired effervescence in fizzy drinks.[25]

CO_2 can also be mineralised and converted into solid forms for use in construction materials, such as aggregates, bricks, or concrete.[26] The carbonation of concrete plays a significant role in the long-term durability and structural integrity of concrete structures. The carbonation process involves the reaction of CO_2 with calcium hydroxide in the cement paste. The mechanism and kinetics are dependent on relative humidity, duration of exposure to water, temperature and CO_2 pressures and concentration.[27] Humidity affects the reaction rate influencing the diffusion and dissolution processes of CO_2 with

calcium. CO_2 pressure during the curing process will directly affect its diffusion rate. Studies have shown that the increase of CO_2 pressure from 0.05 MPa to 0.4 MPa, carbonation increases the strength of concrete up to 34.3%.[28] Similar trends are reported with increasing the CO_2 concentration until the material has reached its saturation point, after which has little effect on accelerating the carbonation process.[28] To evaluate the carbonation of cement, dynamic gravimetric methods can be used to determine the optimum humidity range which will enhance its mechanical properties. The technique can also vary CO_2 pressures and concentrations exposed to cement material as well as observe the effects how temperature can effectively improve the CO_2 sequestration rate. Dynamic gravimetric methods can also be used to measure these essential parameters individually or in combination to reflect real world applications in the carbonation of cement. Examples of the operations of the technique are presented and evaluated in later sections of the paper.

Storage

Alternatively, captured CO_2 can be permanently stored by injecting into secure geological underground porous rock formations such as depleted oil, gas reservoirs and saline aquifers.[29] However, storage potential is not always accessible or commercially feasible. The untapped potential is a result of practical considerations such as technical feasibility, economic viability, environmental and social factors.[29]

Carbonate reservoirs are attractive for CO_2 sequestration as 60% of the world's oil reserves are absorbed in these types of rocks typically found in the middle east.[30] With their proven capacity to retain hydrocarbons, the physical and chemical retention mechanisms for CO_2 secure their long-term storage capacity. The recurring challenge associated with this technique occurs when CO_2 interacts with water in the carbonate rock to produce acidic brine.[30] As a result, the carbonate formation integrity, injectivity, permeability and storage safety is compromised. Research into the CO_2 uptake and storage behaviour of reservoir materials is needed to best understand the immediate technical challenges and long-term capture implications.

Solid Sorbents for CCUS

As innovative technologies are emerging to mitigate the impacts of global warming, it is imperative to address the challenges associated with achieving efficient cost-effective materials for carbon capture methods.

Currently most mature capture technologies typically involve separation using liquid amines via amine scrubbing. The absorption mechanism is based on the amine group - CO_2 chemical interaction[31], through the formation stable carbamates. Once the amine solution becomes saturated with CO_2, the sorbent undergoes a temperature dependent desorption process to release the captured gas.[31] The two major disadvantages of amine scrubbing involve the energy extensive processes and chemical degradation due to thermal regeneration between 120 °C to 150 °C.[32] The second is waste management due to large quantities of hazardous degraded solvent produced as waste through thermal, oxidative and acid gas degradation, which also include operational consequences such as foaming and corrosion and the release of harmful by-products.[32]

A promising alternative to liquid amine sorption are solid sorbents. These are solid materials which can bind CO_2 selectively from a gas stream through surface or bulk sorption. The gas is then recovered by changing the temperature or pressure conditions, which reduces the adsorptive affinity and allows CO_2 to be released. Their potential lies in the energy savings afforded by the lower energy required for recovery, facile handling of a solid phase compared to a liquid, and theoretically faster kinetics from contactor design.

Solid sorbents can be used in all classes of carbon capture technologies previously mentioned making it the most versatile. They can be used as temporary storage media for CO_2 transport, or as functional materials for CO_2 upgrading. The porous rocks in CO_2 storage reservoirs can similarly be considered solid sorbents.[29] Therefore, assessing the real-world performance of these materials in binding CO_2 is of paramount importance to all CCUS areas.

An ideal sorbent must have a high sorption capacity, selectivity for CO_2 with a low heat of sorption and be economically regenerable without significant loss of cyclic performance. The material should undergo multiple uses typically >1000 cycles and have low production costs.[33] The sorbent must be structured with a hierarchical pore structure with a combination of micro and mesopores maximising its surface area and facilitating multiple binding opportunities. However, to be effective there must be strong CO_2-sorbent interactions leading to potential high energy demanding regeneration conditions. Therefore, there is always a trade-off between performance parameters, and it is challenging to meet the desired criteria. Other major challenges include: assessing the kinetics of CO_2 uptake and release at process conditions, determining optimum sorption and activation conditions, verifying the stability of the material throughout multiple cycles, and quantifying the influence of contaminants like water or acid gases on the CO_2 uptake performance.

Analysis of Solid Sorbents used in CCUS

The key evaluation metrics for carbon dioxide capture can be obtained using laboratory gas adsorption measurement techniques, prior to testing and optimising process designs in a pilot plant. Together with collaborators from Imperial College, SMS scientists have summarised an experimental pathway to assess sorbent materials from atomic to pilot scale (Figure 2).[34] The evaluation is based on Key Performance Indicators (KPIs) based on the intrinsic properties of the material, adsorbent performance metrics and process performance. The parameters are related to CO_2 adsorption capacity, selectivity, kinetics, ease of regeneration, stability, adsorbent costs, and environmental impact.[69] A complete characterisation of solid sorbents is paramount for a true understanding of their performance, a conclusion mirrored by numerous other studies and perspectives.[35,36,37,38] Commonly used characterisation methods in the sorption community simply to not offer the whole picture.
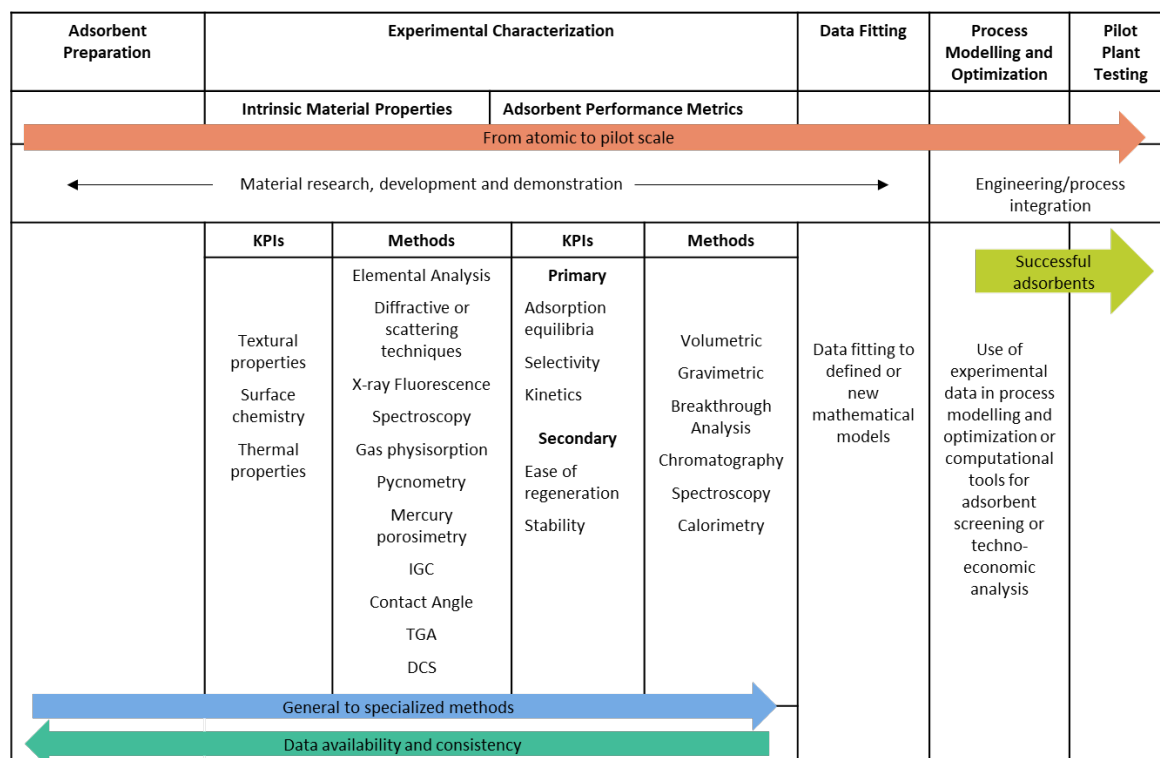

Figure 2. Experimental pathway to assess newly prepared CO_2 capture materials from atomic to pilot scale. Figure reproduced from Saenz Cavazos et al © 2023 Authors.[69]

To screen solid sorbents, it is common practice to record isotherms of pure gases and assess the material's uptake as a function of pressure. This is a useful first step into determining the material's working capacity and stability. Sorption kinetics can also be evaluated at this point, if the instrument can provide it by default, as obtaining diffusion constants is invaluable in process modelling. If a temperature swing adsorption process is targeted, a material's isobar, or uptake as a function of temperature at a constant pressure, is a more relevant metric than an isotherm.

Computational methods can provide unique insights into the mechanism of sorption, including other metrics like uptake and selectivity. However, the computational power required and the often narrow applicability of forcefields and basis sets, limits the amount of information that can be obtained, while other metrics like long-term cyclability remain for now in the experimental domain.

Thermal properties of the sorbent, like heat capacity and thermal conductivity are measured directly through differential scanning calorimetry and temperature profile monitoring, respectively. A common assumption is that the material's thermal properties hold throughout the adsorption process – an assumption which, while necessary due to experimental challenges, often does not hold since contributions from the adsorbed phase (CO_2, water, etc) can dramatically change the full system's thermal properties. Therefore, these properties should similarly be measured at process conditions.

The selectivity towards CO_2 compared to other components of the mixture like N_2, CH_4, H_2O or SO_2 can be intuited from the uptakes of each component in their pure form. However, this approach can only give qualitative rather than quantitative data regarding to selectivity in a real mixture. More rigorous approaches like, IAST (Ideal Adsorbed Solution Theory), use analogues of vapour-liquid equilibria modelling to compute compositions of the adsorbed phase starting from single component data.[39] IAST, while powerful, has limitations, particularly in the case of strongly adsorbing components like water, or when high quality isotherms and fitting models are not available. Ideally, selectivity is determined directly from multicomponent data recorded experimentally, currently one of the biggest open questions.[40] The lack of true multicomponent data is hampered by the availability of instrumentation and the difficulty in conducting quantitative, accurate experiments. The use of packed bed breakthrough analysers (BTA), particularly those optimised for small sample amounts, is practically the only widespread method available for real multicomponent data.

To evaluate material behaviour in real gas mixtures beyond CO_2 uptake experiments, it is important to consider dynamic adsorption studies. This shifts the narrative from the abundantly researched material studies focusing on adsorbent development to the fewer researched process studies. The gap between these studies can be closed by screening

the advanced sorbents in conditions as close as possible to the targeted process. Real gas mixtures must be used instead of just pure components for cycling tests, particularly if the stream will include water or other contaminants. Both BTA and gravimetric methods have been successfully used to test materials in such conditions due to their flexibility in controlling the temperature, pressure and composition of the gas stream while continuously monitoring sample uptake.[41,42,43] Gravimetric techniques have the advantage of high precision testing with extremely low sample amount, from a few mg, leading to faster experiments, even if they only measure the total sorption uptake. Such devices can even be parallelized to offer throughput of up to 5 simultaneous experiments.

Screening of sorbents for carbon capture

Experimental adsorbent screening techniques play a key role in helping researchers comprehensively evaluate the performance and characteristics of solid sorbents for carbon capture. Current successful, complete, and comprehensive analysis involves a collaboration between multidisciplinary laboratories which can be expensive and time consuming. Moreover, such differences in techniques and the combination they are used in, creates challenges in comparing data. The current method used to understand the co adsorption of multiple gas components is using single gas isotherms and applying it to modelling processes.[44] Therefore, there is a desire to use a technique that can measure metrics in a standardised way which can obtain kinetic and thermodynamic data sets to facilitate a comparison between adsorbent materials. The Dynamic Vapour Sorption Carbon (DVS Carbon) instrument can be used to measure such parameters and extensively minimise experimental time and equipment costs.

The DVS Carbon is part of a family of DVS systems developed at Surface Measurement Systems. DVS is a gravimetric technique that measures the mass of a sample as it changes in response to changes in temperature or humidity. The DVS Carbon is the first purpose built gravimetric sorption analyser for advanced carbon capture conditions. It has the unique ability to simulate real-life conditions by controlling both temperature and humidity while measuring the uptake of CO_2. Therefore, it can provide insights into how CO_2 behaves in practical situations.

The schematic of the DVS Carbon is shown in Figure 3. Its symmetrical design minimises flow and drag effects by exposing both the sample and a reference pan to the same conditions. It has a series of mass flow controllers which employ a dry carrier gas which is typically nitrogen or compressed air. It is also connected to a CO_2 supply which can be mixed with the saturated gas and adjusted to a desired flow rate and gas ratios to precisely generate different levels of partial pressure. To imitate real life conditions for

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carbon capture it can provide independent multicomponent control. This is imperative when determining competitive sorption behaviour of CO_2 and H_2O.
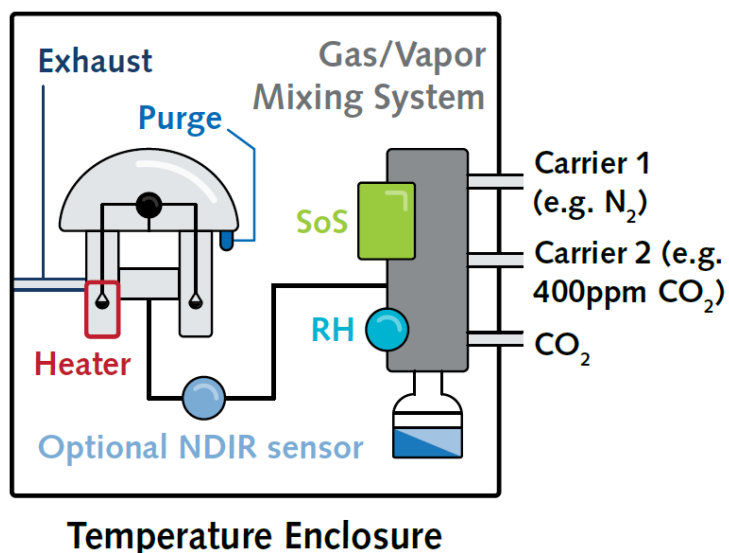

Figure 3. Schematic of the DVS Carbon

The system can also simulate and study the effects of cyclic changes in humidity on a material's moisture sorption behaviour to better understand the capabilities and limitations of a material to undergo multiple rounds of carbon capture. To measure the saturation capacity, the DVS can accommodate for changes of CO_2 at high partial pressures or low ppm ranges. This specification plays an integral part in applications in DAC and CCUS conditions. Activation via local temperature elevation can determine the success of sorption materials at the onset, effecting its capabilities. The DVS system has an *in-situ* activation process which can preheat materials to 300 °C under inert or process gas to determine drying behaviour, conditions for optimal activation and measure regeneration kinetics directly.

Examples of material classes analysed using the DVS Carbon

Metal Organic Frameworks (MOFs)

MOFs have demonstrated potential as effective sorbents for CO_2 capture systems. Ongoing advancements in MOF design and synthesis aim to harness the unique properties of MOFs for efficient and economically viable solid sorbents.[45] MOFs can possess an exceptionally high surface areas and their porous nature allows for rapid diffusion of gas molecules within the material facilitating a higher rate of adsorption and desorption. [46] Their structure can be engineered to have specific pore sizes, shapes and functional groups facilitating interaction, improving the adsorption capacity and selectivity adsorbing CO_2 while excluding other gases.

Nevertheless, the labile metal-organic connectivity means that MOFs can often be sensitive to various factors such as moisture, temperature, and chemical impurities, which may affect their structural integrity and performance over time. [47] As a result, the framework can be susceptible to collapse upon exposure to moisture in the air, thermal and or vacuum treatment.

Researchers are investigating methods to mitigate the impact of moisture, such as incorporating hydrophobic functionalities into the MOF structure. For example, post synthetic modification with long alkyl substituents has shown to be successful[48]. Hydrophobicity promotes the MOF–CO_2 interaction, increasing its adsorption capacity. To ensure the long-term performance of MOFs, researchers are working on optimising the cycling stability by developing regeneration methods that minimise structural damage and degradation during the desorption process. For an efficient capture process, the thermodynamic CO_2 binding enthalpy should be an exothermic process, at least 50kJ mol^{-1} therefore the sorbent material should be thermally robust and withstand multiple sorption cycles without the loss of activity and chemical integrity.[49] MOFs SIFSIX-3-Cu and SIFSIX-3-Ni display strong interaction with CO_2 (enthalpy of adsorption of –56 kJ mol^{-1} and –51 kJ mol^{-1}, respectively), and thus exhibit high CO_2 adsorption capacity at very low pressures, making these MOFs promising candidates for direct air capture.[50,51]

Evaluation of MOFs

HKUST-1 or MOF-199 is a solid sorbent which has demonstrated gas storage properties.[52] Developed in Hong Kong University of Science and Technology (HKUST) in 1999 by Chui and co-workers, its framework consists of carboxylate groups coordinated by copper ions creating 3D porous networks.[53] Doping with Li during post synthesis modification has shown to have a strong affinity to CO_2 molecules.[54] Using pressures of

18 bar at 298 K, the unmodified HKUST-1 has demonstrated a CO_2 adsorption capability of 295 mg/g. Improving its structure by incorporating Li with ratios of 0.07 mol Li to 1 mol of Cu has increased CO_2 sorption to 469 mg/g.[55] HKUST-1 has also been functionalised with amines bound to copper sites. It demonstrated promising CO_2 sorption at 0.2 bar and 35 °C.[92] However, a consequence of amine incorporation results in a smaller surface area of the MOF limiting its sorption capacity at higher pressures. These findings suggest that HKUST-1 has the potential to be commercially feasible in gas adsorption applications. However, the fatal defect of HKUST-1 and MOFs in general is their poor long-term stability in the presence of water vapour attributed to the metal ligand bonds held by weak interactions. Gul-E-Noor et al. studied the decomposition of the material observing the structural changes using ^1H and ^{13}C solid state NMR techniques detecting free coordination sites at the copper centres.[56] Prolonged exposure to high relative humidity or consecutive cycling of water vapour destroys both its crystal structure and reduces its sorption capacity to less than five cycles.[93] The real-world applications of HKUST-1 for its role in carbon capture is critical to its interaction with water as it is inevitable in process conditions. Therefore, it is imperative that solid sorbents undergo comprehensive analysis ensuring all parameters are measured which relate to real life conditions.

MOF materials have been analysed using the DVS Carbon. Two MOF materials were singled out for their promising uptake for carbon capture at post combustion levels, and were selected for further study. Figure 4a shows the CO_2 uptake capabilities of a cobalt-based MOF sample from 25 °C to 40 °C. As expected, adsorption capacity increases at lower temperatures.[57] The isotherms were used to calculate the enthalpy of adsorption with increasing loading of CO_2 (Figure 4b). This MOF shows a relatively flat energy profile, with an optimal enthalpy of adsorption of 30-35 kJ/mol, suggesting sorption sites of equal energy. Both the working capacity and regeneration therefore fall within ideal ranges for post-combustion capture.
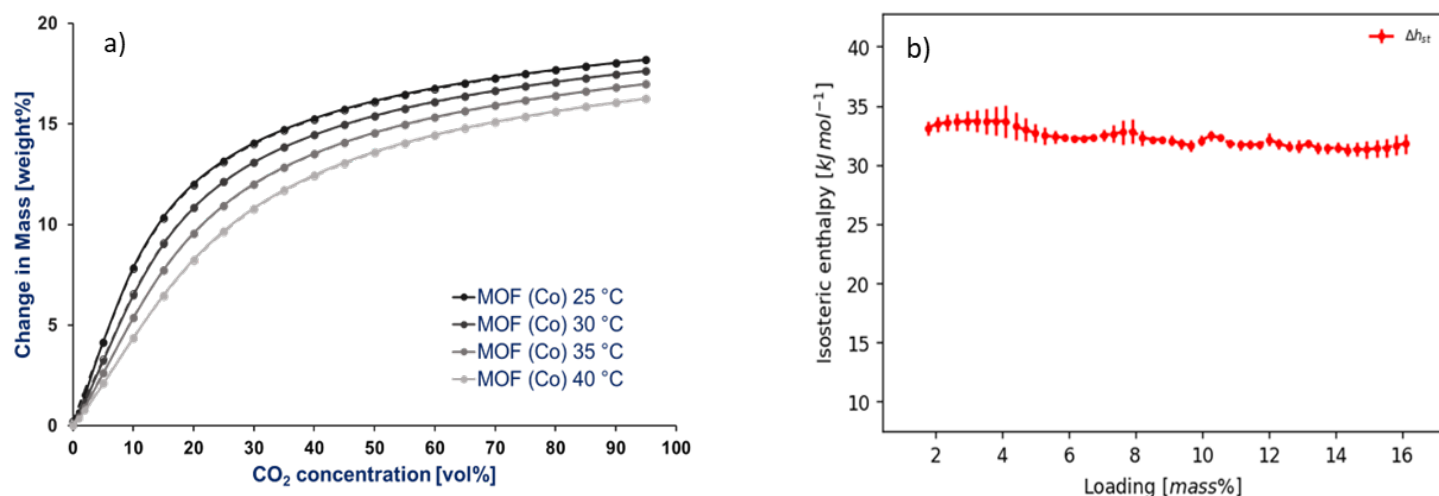
Figure 4 a) CO_2 uptake as a function of temperature for a Cobalt-based MOF sample. Adsorption and desorption are seen as fully reversible b) enthalpy of adsorption of the material

The behaviour of the MOF was then analysed for its co-sorption effect of water at 40 °C and 70 °C with a 20% vol% of CO_2 shown in Figure 5. This experiment ensured a steady flow of CO_2 while introducing up to 75% relative humidity in 5% steps. The results showed that the total sorption capacity was unaffected by the temperature increase however there was a difference kinetic behaviour. Introducing 5% RH at 40 °C caused a faster uptake of water compared to 70 °C. During the desorption process the removal of water molecules was more efficient at a higher temperature however the MOF did not revert back to its original mass which suggests an even higher temperature is required to ensure the material is at maximum capacity to undergo another cycle.
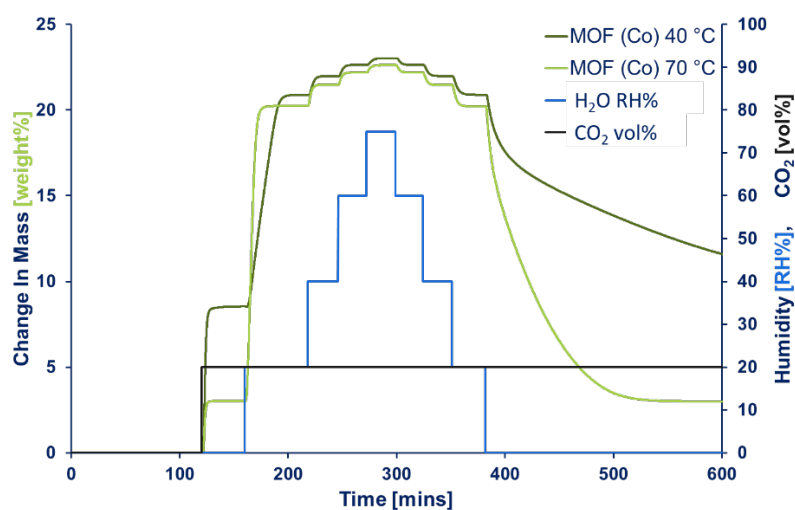

Figure 5. Co-sorption of water at 40°C and 70 °C in the presence of 20 vol% CO_2.

Zeolites

Zeolites are another class of materials that have been explored for CCUS usage. They are silicates consisting of tetrahedral SiO_4^{4-} units interconnected through O-bridges generating 3D crystalline microporous structures. Some Si^{4+} atoms can be substituted by Al^{3+} resulting in a negatively charged framework with large vacant pores where cations act as charge-balancing atoms.[58] CO_2 sorption and preference over other gases is dominated by electrostatic and dipole-dipole interactions.[41] Although in small-pore zeolites diffusion and size exclusion typically play an additional role.[59] The ratio of Si/Al in zeolites can influence its adsorption capacity and selectivity and it has been reported that CO_2 capacity increases with a low Si/Al ratio.[60] However, as a result there is a decrease in pore volume because for each Al site there is a cation interaction causing steric hinderance reducing CO_2 adsorption capacity.[61]

Zeolites generally have a good capacity at low pressures <10bar and low temperatures and reasonable selectivity over N_2 and CH_4.[62] The low cost of most zeolites make them an attractive sorbent for CCUS applications. Nevertheless, zeolite performance can be compromised in the presence of moisture since both H_2O and CO_2 compete for the same adsorption sites.[63] Due to the strong interactions between H_2O and the zeolite framework the regeneration energy required, if the material is water saturated can be very high.[64] In addition, if the zeolite has a low Si/Al ratio some areas will be more susceptible to hydrolysis.[65,66] Other contaminant gases can similarly contribute to the poisoning of the zeolite.[49] The CO_2 sorption behavior of the commercially available zeolite 13X has recently been studied for the removal of CO_2 in low temperature DAC systems.[67] As a low silica zeolite, it preferentially absorbs water from the humidity in gas streams. The activation stage of the DAC process starts off at 350 °C of air in the stream. During the adsorption phase this is bought down to -20 °C at 400 ppm to reduce levels of humidity. A second step is deployed which uses silica gel as a desiccant to remove moister from the air. The desorption step was carried out under 0.1 bar vacuum at 125 °C. This low temperature method offers the potential to reduce energy costs and produce 4359 MJ/tCO_2.[50]

Evaluating Zeolite 13X

Zeolite 13X is a sodium-exchanged aluminosilicate zeolite with a faujasite topology and an effective pore size of around 0.9-1 nm. It is often used in industrial gas separations, such as oxygen production, gas drying or desulfurisation. It has been regarded as a benchmark material for CO_2 capture because of its high CO_2 adsorption capacity, high CO_2 over nitrogen selectivity and good thermal and mechanical stability.[68] In accordance

with most zeolites, it is found to be more effective at ambient temperature as physical adsorption is more predominant and less effective at higher temperatures. These properties make it a promising candidate for post combustion capture technology from flue gases. Unfortunately, it has extremely high affinity for water means that CO_2 adsorption is inhibited in humid conditions, as H_2O competes and occupies the micropores. Trace amounts of water have been shown to increase the uptake of carbon dioxide in zeolites due to new hydrogen bonds being formed which can interact with both the zeolite surface and CO_2 gas molecules.[69] However, a gas flow with a high concentration of water, such as unprocessed flue gas, can result in water getting selectively adsorbed in the zeolite, limiting the uptake of other gas molecules. It is also well-known that water will slowly degrade the typical zeolites and zeolite-binder composite pellets, which will have adverse effects on the gas transport through the bed.[70]

Using the DVS Carbon, individual isotherms of CO_2 and H_2O of zeolite 13X were measured in an inert carrier gas are shown in Figure 6 and Figure 7 respectively. It is important to discuss the shape of the isotherm since materials with the highest CO_2 uptake at 1 bar do not necessarily have the highest uptake at 400 ppm. For example, Mg-MOF-74 has a high CO_2 uptake of 7.95 mmol/g at 1 bar but only 0.088 mmol/g at a CO_2 concentration of 400 ppm.[71] Sorbents with steep isotherms at low pressure tend to have high CO_2 uptake at atmospheric concentrations.[83] The CO_2 isotherm for zeolite 13X is presented as a function of volume gas composition 0% - 95% (vol%), the water isotherm is shown as a function of relative humidity 0% - 95% (RH%). At 100 RH% the gas phase composition by volume of water is around 3 vol%. It is immediately clear that water has a high affinity on the material, with the sample nearly fully saturated even below 1 RH%. The results are consistent and in accordance with literature.[72,73] The CO_2 uptake isotherm shows characteristics of a Type I isotherm. The steady gradient indicates a monolayer adsorption mechanism commonly applied to micro-porous adsorbents. The shape of the water vapour isotherm indicates a type II isotherm which is attributed to the filling of macropores.[85]
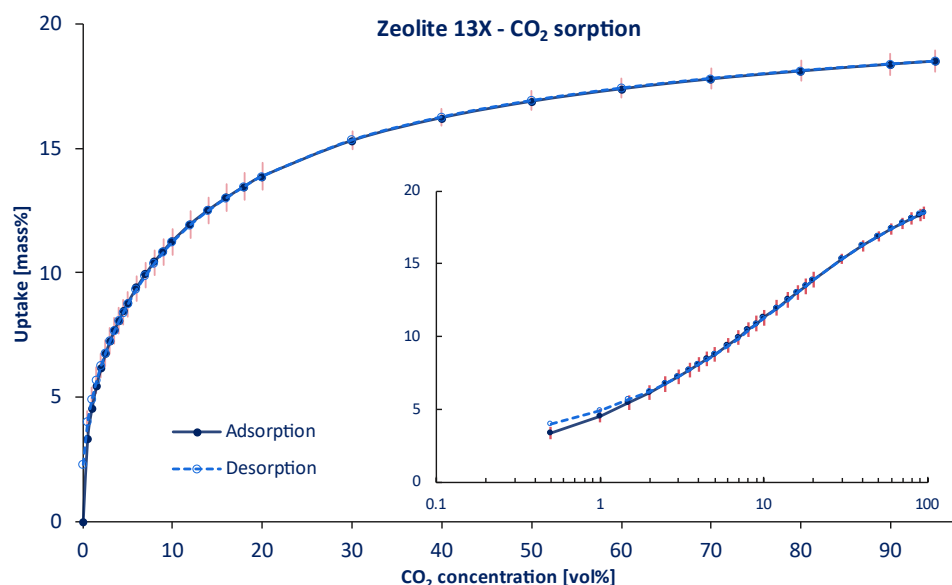
Figure 6: Isotherm of CO_2 at 25°C on Zeolite 13X in a N_2 carrier flow, with adsorption and desorption branches. Error bars are 95% confidence level (3σ) of adsorption branch, based on data from 3 experiments. Inset shows same data on a semilog basis (without 0% values). A slight repeatable hysteresis is visible in the desorption branch, yielding approx. 2.3% irreversible uptake by mass.
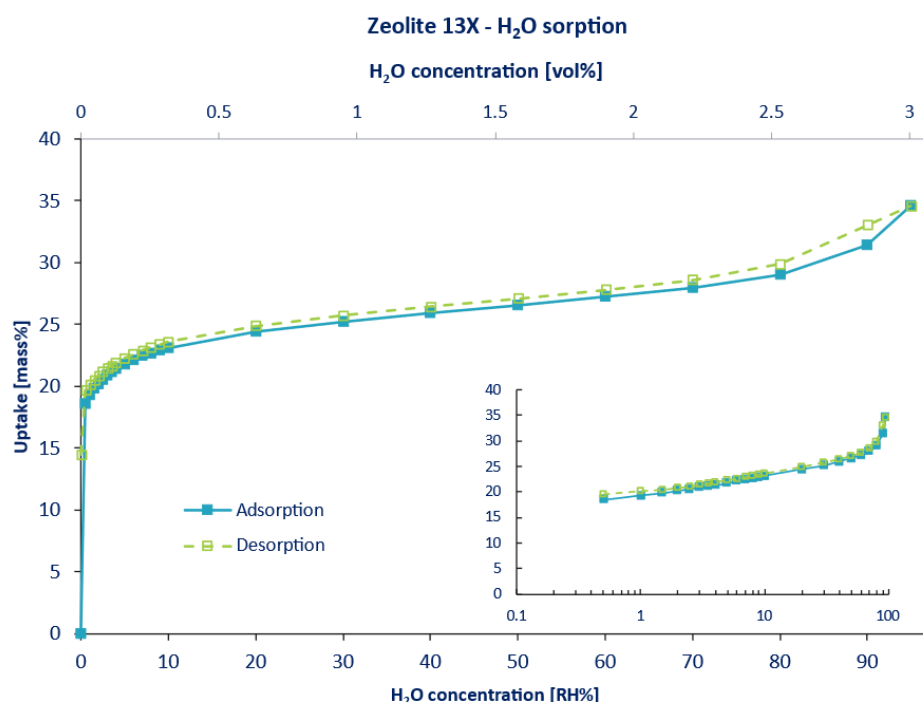

Figure 7: Isotherm of H_2O at 25°C on Zeolite 13X in a N_2 carrier flow, with adsorption and desorption branches. Inset shows same data on a semilog basis (without 0% values).

A large hysteresis is visible in the desorption branch, about 15% mass uptake remains under a dry stream.

Zeolite 13X has been the subject of kinetic evaluations on three separate occasions. Ryu et al. undertook measurements of water vapor at 298 K and 398 K, while adsorption kinetics at 383 K were investigated by Sayilgan et al. Furthermore, Zabielska et al. conducted a comprehensive analysis comparing the studies.[74,75,76] Results showed that the adsorption equilibrium at low pressures corresponded to an irreversible isotherm.[86] Suggesting that high energy input is required to regenerate the materials. Isotherms revealed a higher affinity for water than CO_2. Kinetic coefficients for CO_2 at 20 °C and 74 °C were higher than that for water, suggesting that CO_2 can be adsorbed faster than water vapour and is in competition to access the 13X zeolite surface at lower temperatures.[86] All three studies have obtained results through individual component analysis of H_2O and CO_2. There is a gap in literature data demonstrating two component systems for a more comprehensive analysis.

To observe the water sorption kinetics – experiments were carried out with varying temperatures of 25 °C, 25 °C and 45 °C maintaining the RH at 5%. The kinetics plots in Figure 8 show that at higher temperatures, Zeolite 13X reaches nearly the same water uptake quicker than at lower temperatures.
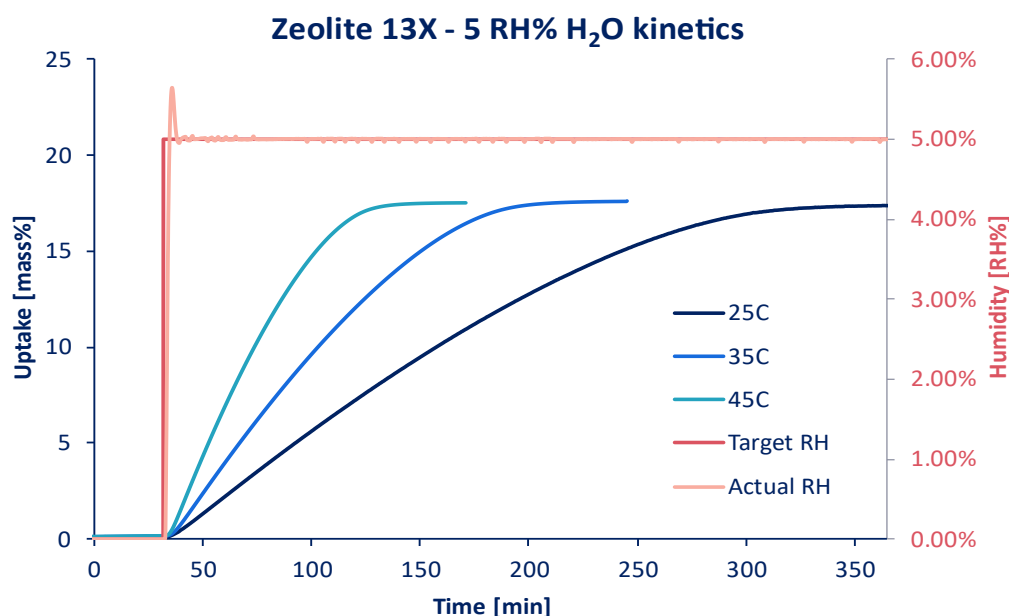

Figure 8: Kinetics of water sorption up to 5% RH on Zeolite 13X at 25°C, 35°C and 45°C.
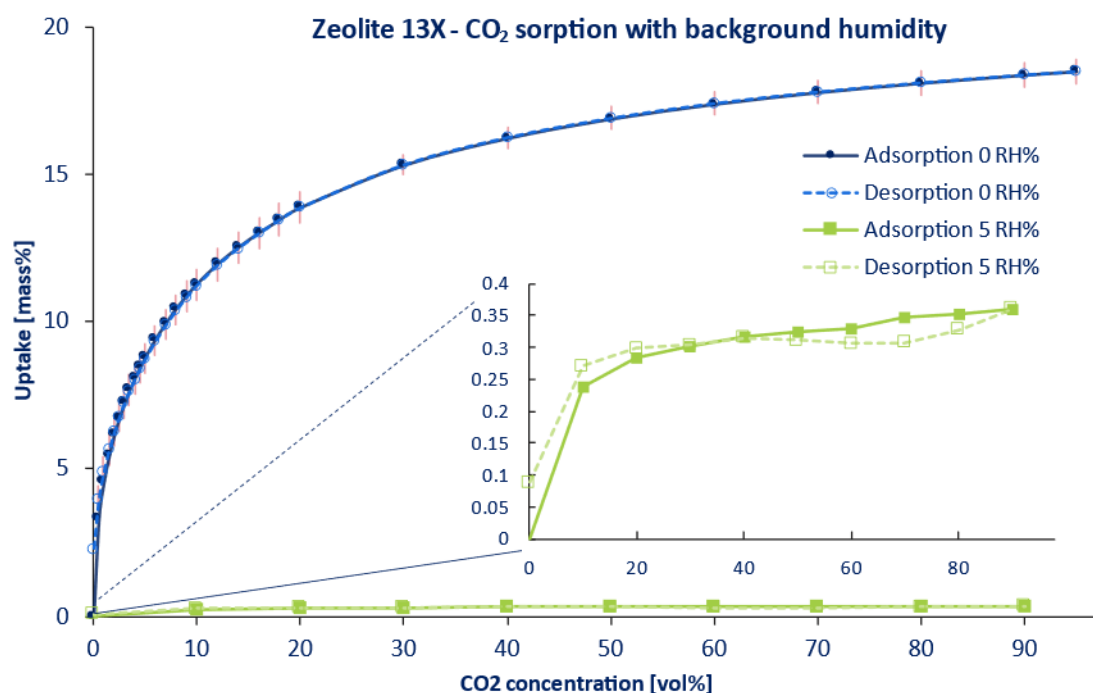
Figure 9. The Impact of constant humidity (5 RH%) on CO_2 capacity at 25°C on Zeolite 13X in a N_2 carrier flow. Inset shows zoom of isotherm with 5 RH%. Sample was activated in situ at 200°C, then pre-loaded with water. Assumes no displacement of water by CO_2.

To investigate multicomponent sorption conditions, a constant flow of inert gas at a 5 RH% relative humidity was used as a background, while varying % volume composition of CO_2 from 0% to 95%. (Figure 9). Under co-adsorption conditions, the introduction of CO_2 induces a negligible increase in mass, highlighting that the sorption sites and pores are already occupied by water even at a low relative humidity of 5%.

Amine Functionalised Sorbents

Amine-functionalised sorbents are governed by amine chemistry in the solid state and are widely investigated for carbon capture applications. These sorbents consist of solid materials, such as porous supports (carbons, polymers, silicas or resins), that are functionalised with amine groups either by impregnation, post-synthesis grafting or co-condensation.[77] Impregnating or incorporating amine groups in the structure of a solid sorbent can overcome the previously mentioned issues of liquid amines through protection against degradation and volatilization.[51]

The amine groups have a high affinity for CO_2 and can selectively capture and bind CO_2 molecules through chemical reactions, typically forming carbamate or bicarbonate species. Long chain amines have been effective functionalised substituents. For example, two widely encountered amines are tetraethylenepentamine (TEPA) [78], a small molecule with five amine groups, and polyethylenimine (PEI) a polymer which can be in branched or linear form. [79]

The performance of amine-functionalised sorbents can be influenced by factors such as the amine loading, porosity, surface area, and stability of the supporting material. These materials are advantageous over porous adsorbents because of their high tolerance against moisture, and even an enhancement effect due to a change in reaction stoichiometry in the presence of water.[80] Nevertheless, it is very important to minimize downsides such as oxidative and thermal degradation, and maximise the kinetics of sorption by sufficient accessibility of amine groups.

Evaluation of an Amine Sorbent

There are some cases where the introduction of water over a sorbent can facilitate an increase of CO_2 capture, as previously discussed for solid sorbents impregnated or functionalised with amines. Lewatit VP OC 1065 has gained attention for its application in DAC.[81] Both CO_2 and H_2O were found to adsorb on the amine active sites present on the pore surface of the sorbent material. The interaction between CO_2 and amine groups were characteristic of chemisorption and the interaction with H_2O showed characteristics of physisorption via a multilayer adsorption. This is reflected in the heat of adsorption: Δ_{H2O} = 43 kJ mol^{-1} and Δ_{CO2} = 70-80 kJ mol^{-1} and capacity.[95] At 95% relative humidity, maximum capacity for H_2O was 12.5 mol kg^{-1} and maximum capacity for CO_2 observed was 2.8 mol kg^{-1} measured at 303K, PCO_2 = 81 kPa.[95]

Amine sorbents have been analysed using the DVS Carbon. Figure 10 shows the interaction of CO_2 on an amine functionalised sorbent. An inert gas flow with 2% water vapour was applied at the beginning and upon saturation, 400 ppm CO_2 was introduced. Introducing 400 ppm CO_2 is comparable to the low concentration of CO_2 in the atmosphere. These experiments are designed to effectively mirror real world conditions for direct air carbon capture. The increase in mass can be assigned to the adsorption of CO2 – even in humid conditions.
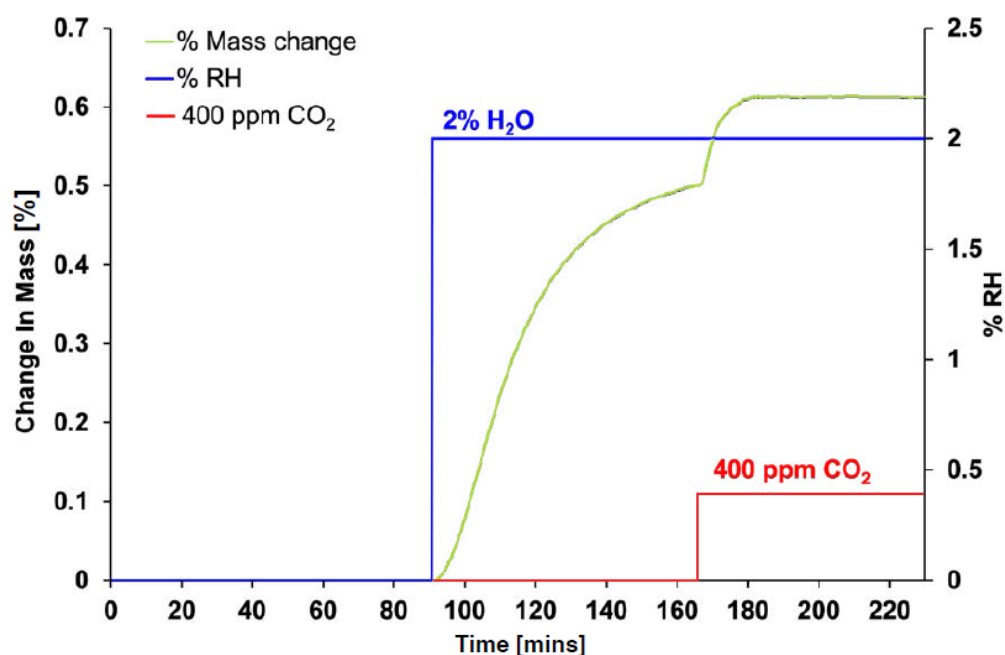
Figure 10. Kinetic plot of CO_2 uptake at atmospheric levels of an amine functionalised carbon, with 2% background of relative humidity

Figure 11 shows an example of a series of experiments where an amine support sorbent undergoes an initial exposure of 50% RH resulting in >3% uptake in mass. A desorption step was then performed reverting the material back to its original form. The next step measured the uptake of CO_2 at 400 ppm resulting to a much lower uptake. The final step analysed the effect of co-sorption of both water and CO_2. Here the presence of water enhanced the capability of the sorbent to bind to more CO_2 optimising the materials sorption capacity. The interaction with water and amine molecules created new sorption sites and binding capabilities available for carbon capture. This behaviour was also observed during co-adsorption studies of CO_2 and H_2O on Lewatit VP OC 1065. Results showed that CO_2 capacity was higher in the presence of water. This was a consequence of water acting as a free-base forming bicarbonate ions whereas in dry conditions carbamates are formed.[95] Therefore, where in dry conditions two amine molecules are required to interact with one CO_2 molecule, in the presence of water, only one amine group can interact with one molecule of CO_2.[95]
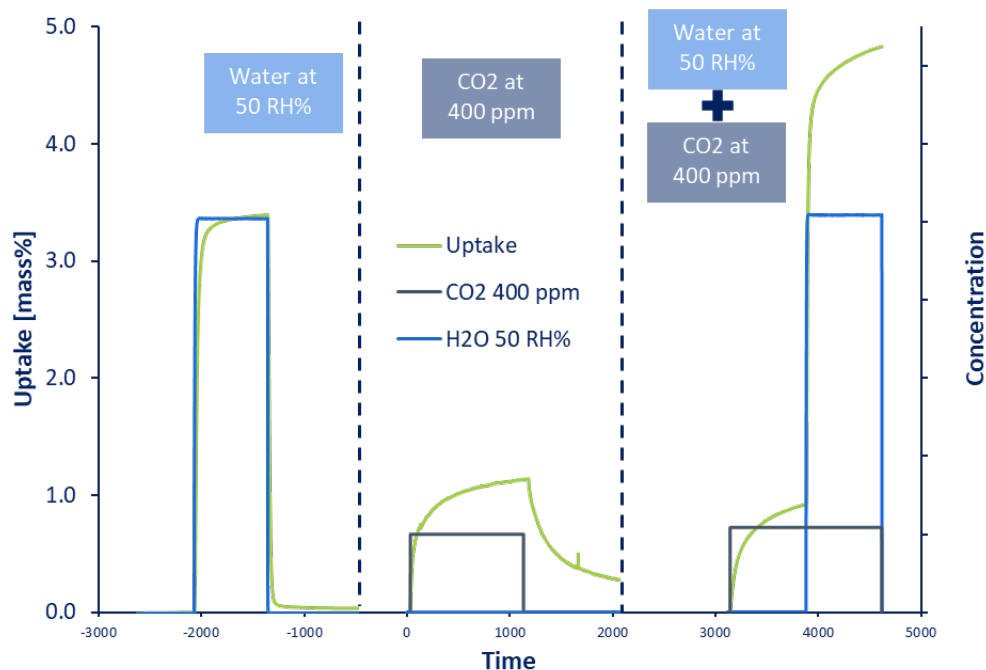
Figure 11. Sequential experiments evaluating kinetics of adsorption during step changes in humidity, 400 ppm CO_2 and both components

Processes for employing solid sorbents

Pressure Swing Adsorption

The regeneration strategy of sorbent capture can be accomplished by either Pressure or Temperature Swing Adsorption (PSA and (TSA). This is achieved by either increasing and decreasing pressure, or temperature or a combination of both. PSA is a cyclic adsorption process, by periodically changing the pressure of the system to achieve the removal of contaminants from flue gases. The PSA process begins at the inlet where the flue gases are introduced. This chamber is pressurised at over 3 atm resulting in CO_2 adsorption.[82] Once the sorbent has reached its capacity, the system is pressured back to 1 atm releasing CO_2 under a continuous purging gas stream. The performance of PSA is evaluated by purity and recovery. The choice of sorbent is critical to the success of PSA. The material needs to have good recyclability over several swing cycles and be stable towards CO_2 at both high and low pressures, correlating to adsorption and desorption respectively. Different sorbents require different pressure profiles but are typically around 10–30 bar in the adsorption cycle.[83] To be cost effective it needs to relatively cheap and provide a

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high CO_2 generation. It is often the case that sorbents with a high CO_2 capacity yield a favourable adsorption isotherm but as a result its desorption isotherm is unfavourable therefore suffering from poor regeneration ability.[84] Due to these two conflicting tendencies, it is difficult to determine which sorbent is suitable for PSA. Both zeolites and activated carbons are effective candidates for this technique.[85,86] While this process is effective it has a few drawbacks.[87] One of which is its short cycle times resulting in "switch losses" which is a loss of feed gas during the depressurisation step. The short cycle time can also change the inlet flow leading to unstable pressures. Also, when the process is operating at low pressure it can leak impurities into the gas stream which can have a stronger affinity to the sorption media than CO_2.[60]

Temperature Swing Adsorption

Temperature swing adsorption is also considered a promising technique which uses moderate adsorption heat between 25-50 kJ/mol enabling the use of low-grade heat sources.[88] During this process the flue gas at ambient temperature and atmospheric pressure, is subject to an adsorption step capturing CO_2 typically at 40-60°C.[89] Upon saturation of the sorption bed, it is heated up following a desorption step typically between 120-150°C.[90] During regeneration, the pressure increases inside the system ejecting a high purity stream of CO_2. This is followed by a N_2 purge resulting in an increase of CO_2 recovery. The system is then cooled down back to ambient temperatures before the subsequent cycle. [91] A disadvantage of the process is that it requires a pure stream of N_2 to heat the adsorbent, effectively diluting the CO_2 stream. This can typically be overcome using heat exchangers indirectly heating the sorbents with the consequence of applying an additional energy cost.[92] The use of zeolites, MOFs, activated carbons and Microporous Organic Polymers (MOPs) have been mainly used in the temperature swing approach.[93,62] TSA is recognised to be more appropriate for post-combustion CO_2 capture since it can remarkably reduce the energy requirement for CO_2 capture by avoiding the compression or application of vacuum to large volumes of a low-pressure gaseous stream needed in PSA.

Moisture Swing Adsorption

The core principles of moisture swing adsorption involve the cyclic alternation between wet and dry conditions, creating an environment where CO_2 is preferentially adsorbed during dry conditions and released during wet conditions. Wang et al. studied the moisture swing technique using an anion exchange resin sorbent that carries carbonate ions for CO_2 adsorption.[94] The mechanism was based on the reversible hydrolysis reaction of carbonate ions in confined nanopores, driven by the evaporation of water.[95] The unique characteristic of this moisture swing sorbent is that it can achieve high affinity

for CO_2 when the surroundings are dry (during water evaporation), and it releases the captured CO_2 when wet. This moisture swing process allows for low CO_2 adsorption heat of around 32 kJ/mol, as opposed to the traditional thermal swing process, which requires higher energy input.[68] This moisture swing sorbent has been primarily proposed for capturing CO_2 from ambient air, particularly in situations with extremely dilute CO_2 concentrations, around 400 ppm from small emission sources.[68] The low energy-cost nature of this sorbent makes it suitable for capturing CO_2 from various gas stream sources with larger CO_2 concentrations. The moisture swing technique offers potential advantages in terms of energy efficiency and adsorption/desorption cycles compared to traditional thermal swing processes. Further research and development may explore its applicability in different carbon capture scenarios, including more concentrated CO_2 streams from industrial processes or power plants.

Process requirements emphasize the importance of a material to undergo multiple cycles while maintaining its structural integrity. The ease of regeneration and stability of the sorbent determines the efficiency, cost and feasibility of the process. To this end, the second MOF was subjected to multiple cycles of CO_2 sorption, with increasing moisture conditions, mirroring real world conditions using the DVS Carbon. Figure 13 shows the resulting experiment. First, 7 cycles of pure CO_2 sorption are tested. The material shows fast adsorption kinetics and a high capacity of CO_2. The system then introduces various concentrations of water vapour between CO_2 sorption cycles. Water vapour is introduced at 25% RH, 50% RH, 75% RH, and 90% RH. When exposed to lower levels of relative humidity, there is little effect on the sample total capacity. A small amount of water appears to remain trapped in the sample, preventing full reversibility, though less than 5% of total capacity. However, at 75RH we observe a significant decrease in CO_2 capacity and much slower kinetics. Above 90% a large mass increase is observed, with slow extremely kinetics. Further exposure to CO_2 does not induce any appreciable change in mass. This suggests the collapse of the material under prolonged exposure to water. This is an effective experiment as it highlights the moisture limitations with the material and can be used in research studies to identify the effective humidity range of the material.
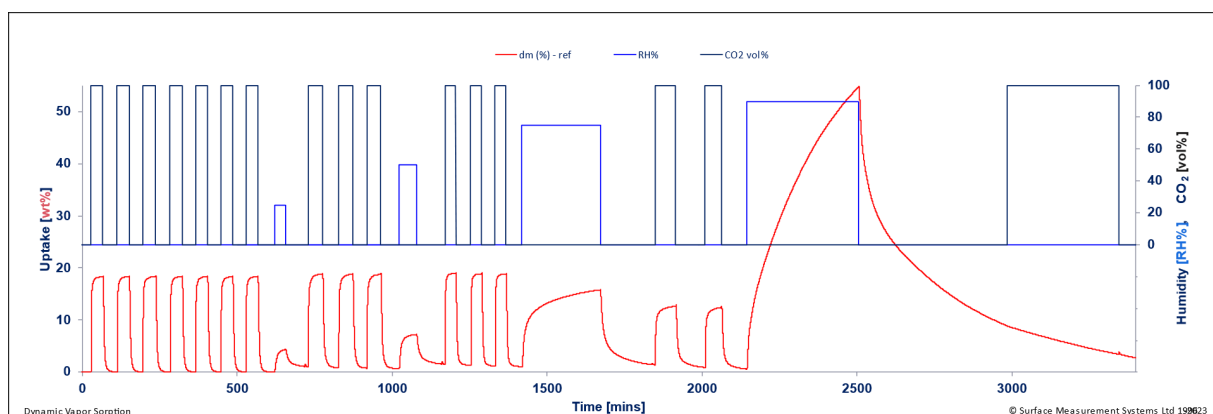
Figure 12. MOF material undergoing a cycling regeneration experiment where the sample was subjected to multiple cycles of CO₂ sorption before introducing water vapour. The levels of relative humidity introduced was 25RH, 50RH, 75RH and 90RH.

Conclusions

The momentum behind carbon capture technologies continues to thrive as awareness and a sense of global urgency to tackle the effects of global warming are becoming prioritised. The field continues to grow with significant progress in research and carbon capture facilities in counties around the world. Ambitious targets have been set by international corporations to offset carbon emissions. As a result, more time and resources are fuelling applications of carbon capture utilisation and storage projects such as carbon sequestration, direct air capture, temperature or pressure swing sorption and solid sorbent characterisation. Solid sorbents act as a vessel where interactions with CO_2 take place. High sorption ability, selectivity, high structural stability, and recyclability all contribute to an effective successful material for carbon capture. These measurable characteristics are commonly analysed using a variety of different instrument and experiments. The DVS Carbon system has proved to overcome the need for different techniques by providing a platform to carry out multiple experiments in one system in a dynamic environment. It is able to recreate real life carbon capture conditions with direct uptake and co-sorption analysis. It can also be used to expose sorbents to multiple cycles of carbon capture at different temperatures to understand the effects of saturation and evaluate its recyclability.

For more information on material characterization
solutions for Carbon Capture, visit
www.SurfaceMeasurmentSystems.com

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