An Overview of Surface Measurement Systems Solutions for Gas Capture, Separation and Storage

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The objective of this overview is to demonstrate the application of SMS sorption solutions as characterization techniques for several research and industrial applications for gas capture and storage. Multifunctional porous materials such as activated carbon, zeolites, silicas and metal-organic frameworks (MOFs) have been considered.

Introduction

The use of solid sorbents for gas capture, separation and storage has potential to alleviate challenges in energy efficiency, climate change and sustainability[1]. In particular, the accumulation of greenhouse gases like CO_2 has become a global priority, in order to achieve decarbonization targets that will allow humanity to attain net carbon neutrality.

Characterizing promising materials for these applications is often challenging, as most experimental studies rely solely on pure equilibrium isotherms rather than actual process compositions and conditions. For example, actual flue gas or ambient air mixtures found in post-combustion and direct air capture conditions respectively, contain a significant amount of H_2O and other compounds such as SO_2 and NO_X, which compete with CO_2 for the adsorbent active sites. Moreover, studying the regeneration, reusability and cyclability of these materials is paramount, alongside the detailed kinetics of the capture process.

There are a number of different sorption measurement configurations available, for example, gravimetric and volumetric methods, ambient flow and vacuum methods, static vacuum and dynamic vacuum methods. This overview note summarises relevant characterization methods for multifunctional porous materials such as activated carbon, zeolites, silica adsorbents, and metal-organic frameworks (MOFs) and their functionalized or modified analogues.

Measurement methodology

a) Static and Dynamic Methods

Static methods

Traditional sorption measurements are conducted in a static, or equilibration mode. In this process, the gas is dosed into a sample chamber containing the sorbent. The chamber is then sealed, and pressure is equilibrated. The method is best suited to adsorbates with fast kinetics (e.g., N_2 but not H_2O). The primary limitation with static measurements is that measurement errors compound with each dose. Also, during the experimental period, the system pressure can

change for various reasons besides adsorption, more commonly due to vacuum leaks or temperature changes. This may lead to errors in measurements, especially at low partial pressures.

Dynamic methods

In the dynamic method, a continuous flow of gas or vapour is passed over the sample. The method controls both the upstream rates of entry and the downstream exit rate, effectively controlling the total pressure/concentration and flow rate of the adsorbate in the chamber. Dynamic methods offer a few benefits over static methods such as better protection from leakage effects and increase sorption kinetics from directed flows over the adsorbent. The principle of dynamic method is illustrated in Figure 1 below.
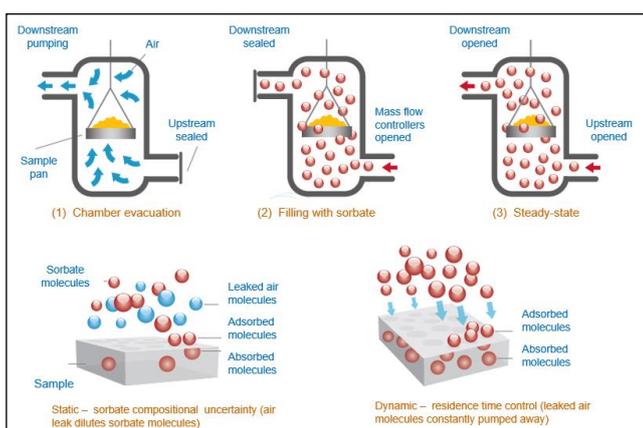
Figure 1. Principle of dynamic vacuum method.

b) Volumetric, Gravimetric and Breakthrough Methods

Gravimetric methods

In a gravimetric method, the change in weight resulting from adsorption is directly measured using a highly sensitive microbalance. The net force can then be equated to uptake, either directly or with a buoyancy correction. Gravimetric measurements are some of the most accurate means of measuring uptakes of gases and vapours in a wide range of conditions.

A well-known benefit of gravimetric methods is that they typically require a low amount of sample: as little as 1 mg can be used to obtain reliable results for single-component measurements. Another advantage of gravimetric systems is that they can be used in both static and dynamic modes.

The SMS DVS Vacuum system is a symmetric balance gravimetric system, which offers unprecedented flexibility for studying adsorption processes under sub-atmospheric pressure, with up to two simultaneous samples.

Volumetric methods

In volumetric methods, a cell containing the adsorbent material is dosed sequentially from a known volume of gas. The parameter measured directly in a volumetric system is pressure change, which is then converted to uptake using an equation of state. Due to this indirect measurement, gas or vapour pressure measurement is not as accurate and sensitive as weight change measurement. To obtain the same sensitivity, volumetric method needs much more sample, which takes longer time to reach sorption equilibrium. Samples can be expensive in some cases, e.g., drug samples for formulation research, this may substantially increase experimental costs.

The volumetric method is by definition a static process, with the associated drawbacks, particularly difficulty in equilibration at low pressures. It should also be noted that each subsequent dose after the first propagates errors in previous doses, such that the uncertainty range after tens of points can become larger than the uptake itself.

Breakthrough methods

In a breakthrough analysis (BTA) method a known gas mixture is passed through a fixed bed or material, and the concentration is monitored at the end of a packed column of adsorbent. The shape of the resulting breakthrough curve provides equilibrium, bed transport and kinetic information. It is one of the few methods which can be used to determine true multicomponent adsorption data: e.g., individual uptakes of two or more components in a mixture.

The BTA Frontier system (commercially available Q_1 2024) is the SMS flagship BTA analyser, consisting of three main sections: generation, bed,

and detection. In the generation section, the desired mix of gases is prepared at a constant flowrate: CO_2, H_2O and/or volatile organic compounds (VOCs) are feasible in a carrier gas (e.g. N_2). The mixture of gases then enters an adsorbent packed column, previously activated in-situ. The concentration profile of each gas is monitored at the exit of the column by a suite of independent detectors.

Pure Component Isotherms

Pure component isotherms are the first step in the characterization of a porous material, assessing the uptake of the component(s) of interest as a function of pressure. This step indicates whether the material has the potential to be competitive for the target application compared to other benchmark materials. Key performance indicators such as capacity, working capacity, enthalpy of adsorption and kinetics can be determined from the isotherms.

a) CO_2 sorption on MOFs

Metal organic frameworks (MOFs) are crystalline clusters of metal ions connected by organic linkers. Their tuneable pore sizes and large specific surface areas (up to 5,000 m^2/g) can facilitate high-capacity storage, or selective separation of CO_2, natural gas, hydrocarbons, hydrogen and other compounds.
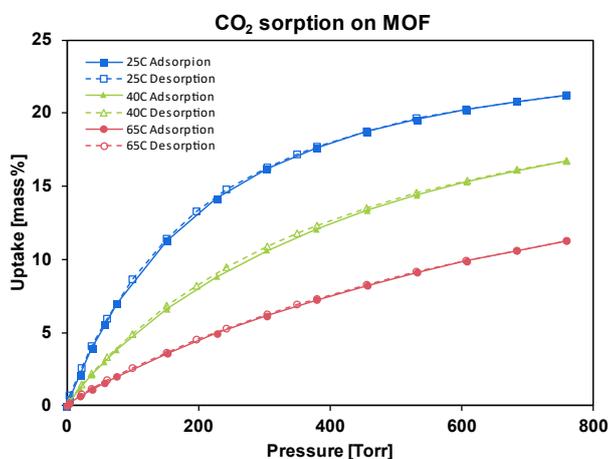
Figure 2: CO_2 gas sorption on MOFs

Figure 2 shows the pure sorption/desorption isotherms of CO_2 on a prototypical MOF at three different temperatures, up to 1 bar (760 torr). This range is highly relevant for both point source and direct air capture, as the concentrations in these applications reach 0.04-50% CO_2 by volume at atmospheric pressures. The isotherm can be then fitted with a model, like Langmuir or Sips, to obtain fundamental parameters that are crucial for process modelling, like simulating beds for PSA or TSA processes.

The isotherms can also be used to determine the enthalpy of adsorption, a parameter representative of the interaction strength of the gas with the adsorbate. Higher interactions mean better selectivity towards CO_2 compared to other gases in the mixture. From a process perspective, the enthalpy of adsorption can be related to the amount of heating in the bed, but also of the amount of energy required to regenerate the material. The enthalpy of adsorption of the previous MOF is calculated using the Clausius-Clapeyron method implemented in the DVS Advanced Analysis module in Figure 3.
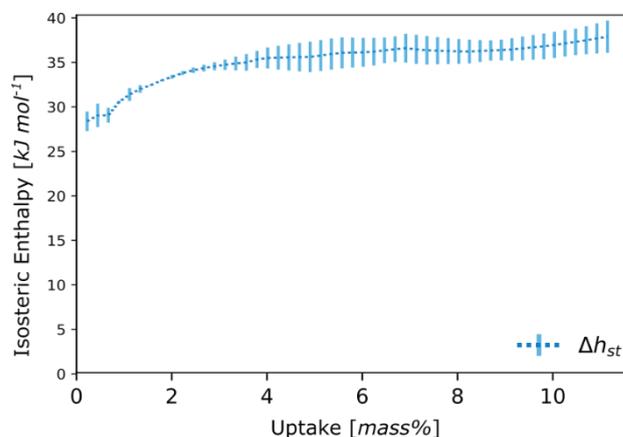
Figure 3: Enthalpy of adsorption of CO_2

b) SO_2 sorption on zeolites at 25°C

SO_2 is a common contaminant in natural gas or flue gas streams, with a high potential for human and environmental toxicity. Scrubbing it through highly selective, yet still reversible adsorption processes would represent an important milestone. In parallel, mass- or electrical- sensors enhanced with porous materials can facilitate its detection even at *ppm/ppb* concentrations [2].

Figure 4 shows the sorption of SO_2 gas on three different prototypical zeolites. The sorption behaviour was found to be highly variable at 25 °C. While the uptakes at saturation are all between 20% to 35% weight by mass, the isotherm shape and reversibility are different. Zeolite 5A has the steepest uptake at low pressure, with more than 15% of SO_2 sorption being irreversible under vacuum. This would make the material a good candidate for SO_2 scrubbing. On the other hand, the adsorption on Zeolite H-SDUSY follows a type V isotherm and is nearly reversible. If used as a catalyst in an acid stream, it may be less likely to be poisoned by SO_2.

in isolation, it is still difficult to determine with certainty the proportion of adsorbent absorbed. However, co-sorption as seen in these studies can be used to give an indication of a material's preference to sorption of one species over another.

a) CO_2/H_2O binary system in a static mode

In a static mode, the two components are introduced sequentially. The sample is first allowed to equilibrate under one adsorbate at a desired pressure. Afterwards, a controlled dose of a second adsorbate is added to the headspace.
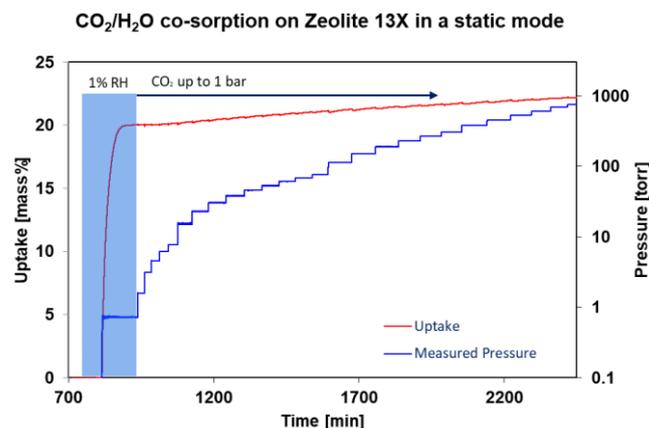
Figure 5: CO_2 adsorption on humid Zeolite 13X

This approach is used to study the total uptake of CO_2 in humid Zeolite 13X at 45 °C. The zeolite was activated under a vacuum of 10^{-5} Torr at 250 °C for 4 hours. The first step in Figure 5 represents dosing of water vapour at a pressure of 0.73 Torr, or 1% RH. The sample takes up almost 20% by weight of water. CO_2 is then incrementally dosed up to a total of 1 bar, or 760 torr. The sample takes up a further 2% of mass.

Single-component measurements in literature[3] show that Zeolite 13X has a CO_2 capacity of around 15 wt% at 1 bar, and a H_2O capacity of approx. 20 wt% at 1 RH%. The, above data clearly shows that the two components compete for the same adsorption sites, as the total uptake is not the sum of individual components.

Figure 4. SO_2 gas sorption on three prototypical zeolites

Two-Component Adsorption

While single component isotherms can be used as a basis for modelling sorption behaviour in a two-component system, exploring the influence of one component on another provides a new level of information regarding the performance of a material for capture or separation.

Using the DVS Vacuum's dual inlets, two components can be introduced, either sequentially or simultaneously. In the following examples we will explore these options.

Most direct measurements of co-sorption experiments come with the same challenges, one being how to interpret or deconvolute the resulting data. Even when comparing co-sorption data with isotherms measured with each adsorbent exposed

b) CO₂/H₂O binary system in a dynamic mode

In dynamic mode, both components are introduced simultaneously. The flow of the two components over the sample will achieve a target pressure in the headspace and the sample equilibrates in mass at a variety of these predetermined pressures. **DVS Vacuum** was used to measure the sorption and co-sorption properties of Zeolite 3A using a dynamic flow of the adsorbate(s). The zeolite was activated under a vacuum of 10^{-5} Torr at 300 °C for seven hours. The sorption measurements were then conducted at 25 °C.

Figure 6 shows the adsorption and desorption isotherm for CO_2 sorption with the uptake measured at 90% P/P_0 being 9.9% of the dry mass. The results for co-sorption from a CO_2 and H_2O flow (~10:1) are also displayed and show a significant increase in uptake: 24% of the dry mass at 90% P/P_0.
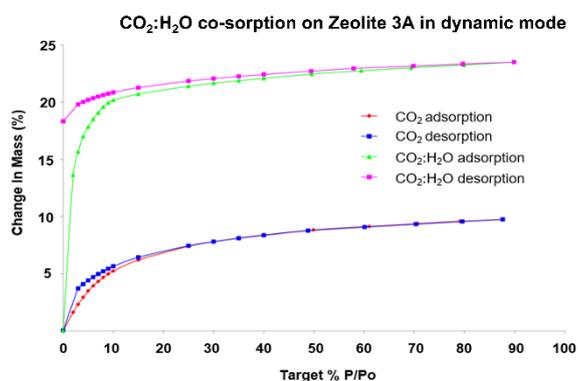
Figure 6: CO_2 sorption and Co-adsorption of CO_2 / water (10:1) sorption on Zeolite 3A

The significant increase in uptake in the co-sorption experiment compared to the single-component experiment demonstrates this material's selectivity for water sorption over CO_2 sorption.

Realistic Process Conditions

To fully understand the material performance for gas capture or separation, experiments should be performed in realistic process conditions, with a close approximation of the gas stream. For example, in CO_2 capture applications, this stream should ideally contain nitrogen, carbon dioxide and

water. Cycling studies in these conditions can also evaluate long-term performance. Both **DVS and BTA** are crucial tools in this endeavour, as will be shown in two case studies.

a) DVS in realistic conditions

The **DVS Carbon** system was used to measure and analyse adsorption and co-adsorption of low concentrations of CO_2 and H_2O on two MOF samples MIL-101(Cr) and a partly functionalised analogue MIL-101(Cr)-4F (1%), respectively at ambient pressure and temperature (298 K and 1 bar), to represent point source capture conditions[4].
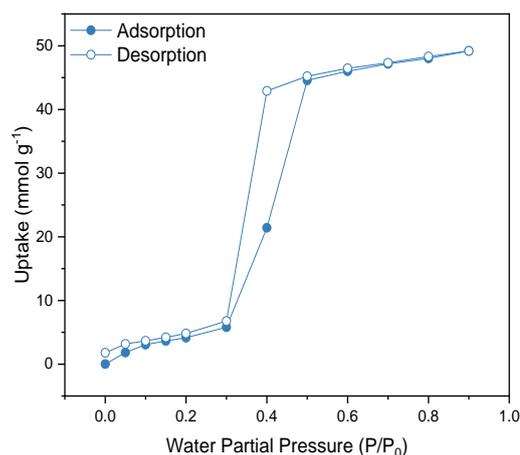
Figure 7. Water adsorption and desorption isotherms of the functionalised material MIL-101(Cr)-4F (1%)

Figure 7 shows the water adsorption and desorption isotherms of the functionalised material. The isotherms correspond to that of a mildly hydrophobic mesoporous solid or Type V, where multilayer adsorption is observed at low partial pressures 0 to 0.3, followed by a clear hysteresis loop between 0.3 and 0.6 that can be associated with capillary condensation taking place in the mesopores. The maximum water uptake for the fluorinated MIL-101 was 49.1 mmol g^{-1}, which is lower to the one reported for the as received material under the same conditions (55.5 mmol g^{-1}).[1] This proves an effective overall hydrophobicity that can be attributed to the incorporation of fluorine atoms [5].

Figure 8 shows CO_2 adsorption isotherms of both materials. The uptake is very similar up to 0.6 bar, but at higher partial pressures the normal MIL-101(Cr) material shows a slightly higher CO_2 uptake. This can be attributed to the lower pore volume of fluorinated MIL-101 compared to normal MIL-101(Cr), 1.19 cm^3g^{-1} and 1.32 cm^3g^{-1} respectively.
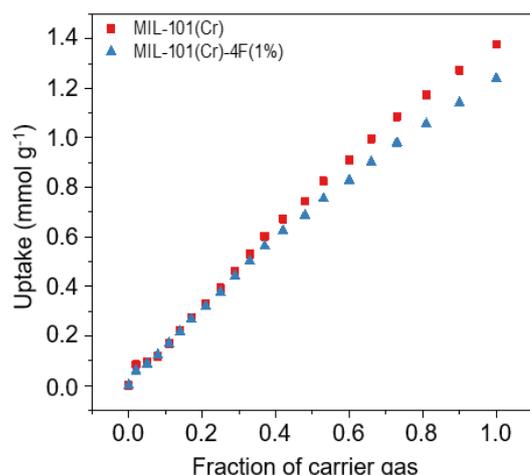
Figure 8. Carbon dioxide (CO_2) adsorption isotherms at 298 K and 1 bar of MIL-101(Cr) and MIL-101(Cr)-4F(1%).

The effects of low concentration CO_2 sorption and diffusion under humid conditions on both materials were measured in the DVS Carbon. Following activation, samples were exposed to a selected range of partial pressure of water vapour to simulate flue gas composition (P/P_0 of water of 0, 0.05, 0.1, 0.15 and 0.2). While this pressure was held constant, a step increase in CO_2 concentration to 0.05 bar was introduced, followed by desorption of CO_2 and finally desorption of water vapour.

The data obtained from a typical co-adsorption experiment consists of four steps, two for adsorption and two for desorption (Figure 9).
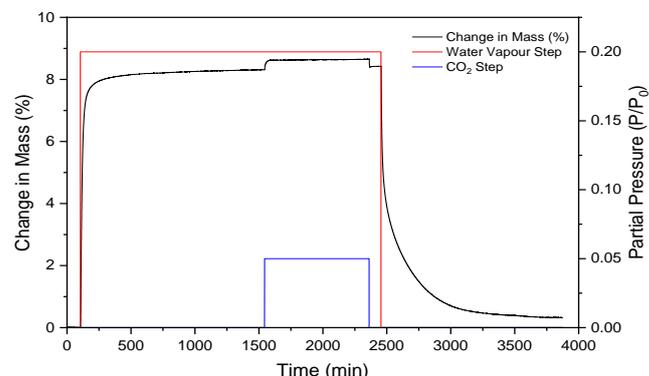
Figure 9. Adsorption and desorption mass change of MIL-101(Cr) exposed to a step change of water partial pressure of 0.2 P/P_0, followed by a CO_2 partial pressure step change of 0.05 bar at 298 K and 1 bar total pressure.
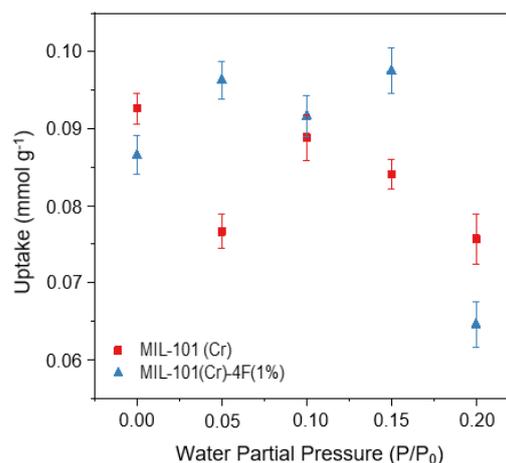
Figure 10. Carbon Dioxide (CO_2) adsorption capacities of MIL-101(Cr) and MIL-101(Cr)-4F(1%), CO_2 P/P_0 = 0.05 at different water partial pressures (0, 0.05, 0.1, 0.15 and 0.2 P/Po) at 298 K and 1 bar.

Figure 10 shows the CO_2 adsorption capacities of both materials at 5.0% CO_2 concentration with different water loadings from 0-0.2 or 0-20% RH.

For the non-modified MIL-101(Cr) the presence of water is detrimental for its performance. CO_2 capacity decreases with increasing amounts of water vapour, up to the highest value studied, where its uptake decreases by around 18% compared to the dry material. On the other hand, fluorinated MIL-101 shows a CO_2 uptake enhancement at low and moderate water loadings, reaching a maximum uptake of approximately 0.1 mmol g^{-1} CO_2 at a partial pressure of 0.15. Nevertheless, at the partial pressure of 0.2, the

fluorinated material shows a 22% lower CO_2 uptake compared to the dry material. This could be because during the activation of the material some terminal water molecules might be lost. However, the complete loss of these water molecules means that some favoured CO_2 adsorption sites may be lost as well. Now, with increasing RH values, some of these adsorption sites are recovered and therefore, the uptake improves. There is a value of RH where the presence of H_2O molecules has no longer a positive effect, and rather, these molecules compete for adsorption sites with CO_2. This phenomenon has been previously reported for other MOFs such as MIL-100 and UiO-66.

b) BTA in realistic conditions

All co-sorption experiments until now could only give an indication of the influence of the presence of one component on another. To fully determine the individual uptakes of multiple components, use of breakthrough methods is required.

A column was prepared of shaped Zeolite 13X pellets, with a total mass of 0.26 g. The **BTA Frontier** is designed with small sample amounts in mind, allowing quick screening of materials for co-sorption conditions.

After activation at 250 °C under an inert gas flow, a mixture of CO_2 and H_2O and nitrogen carrier totalling of 50 sccm was passed through the column, at concentrations of 3.5 vol% and 20 RH%, respectively. Concentration at the column outlet was monitored with the integrated BTA sensors, yielding the breakthrough curves in Figure 11. A blank measurement was performed using helium as an inert gas and then subtracted from the curves to remove contributions of dead volume and axial dispersion. The measurement was repeated in triplicate, with activation between each run.
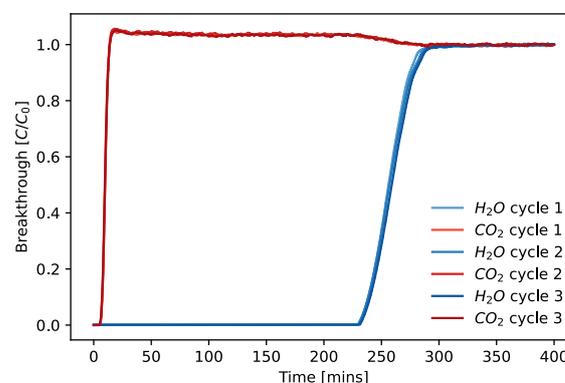
Figure 11: Three repeated breakthrough curves of CO_2 (3.5%) and H_2O (20% P/P_0) on a sample of Zeolite 13X

We observe a relatively fast CO_2 breakthrough, after only 15 minutes, and a much slower water breakthrough, of nearly 4 hours. A characteristic "roll-up" effect is observed, as the water is replacing adsorbed CO_2, and leads to a higher outlet concentration than the inlet while the water front is passing through the column. Near-perfect repeatability is achieved over three cycles.

To obtain the adsorbed amount of each component, the curves can be integrated from 0 to 300 mins, when both components have broken through, yielding 0.55 wt% of CO_2 and 23.4 wt% of water.

The previous mass balance is made with two assumptions in mind. First, that the pressure drop over the column is negligible, which is verified using integrated pressure sensors in the BTA Frontier. Second, that the inlet flowrate is the same as the outlet flowrate, a valid assumption at the low adsorbate concentrations used.

Breakthrough experiments are a crucial step towards assessing real-world performance of gas sorption materials.

Conclusion

Gas capture, separation and storage is of significant importance to energy and the environment, and a key driver of research in industry and academia. It is important to be aware of the wide range of sorption characteristics techniques available and to apply the technique which is most relevant for a material and application. Surface Measurement Systems offers a wide range of instruments which can operate in a variety of modes such as dynamic, static, atmospheric flow and reduced pressure. Each of these different operation modes can offer unique benefits in designing experiments to model a wide variety of systems. As world leaders in sorption science, our expertise and techniques can offer solutions to every step of material screening for gas capture applications.

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