Investigating CO_2/H_2O co-sorption in CALF-20 using a new gravimetric-integrated gas analysis method

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1 Introduction

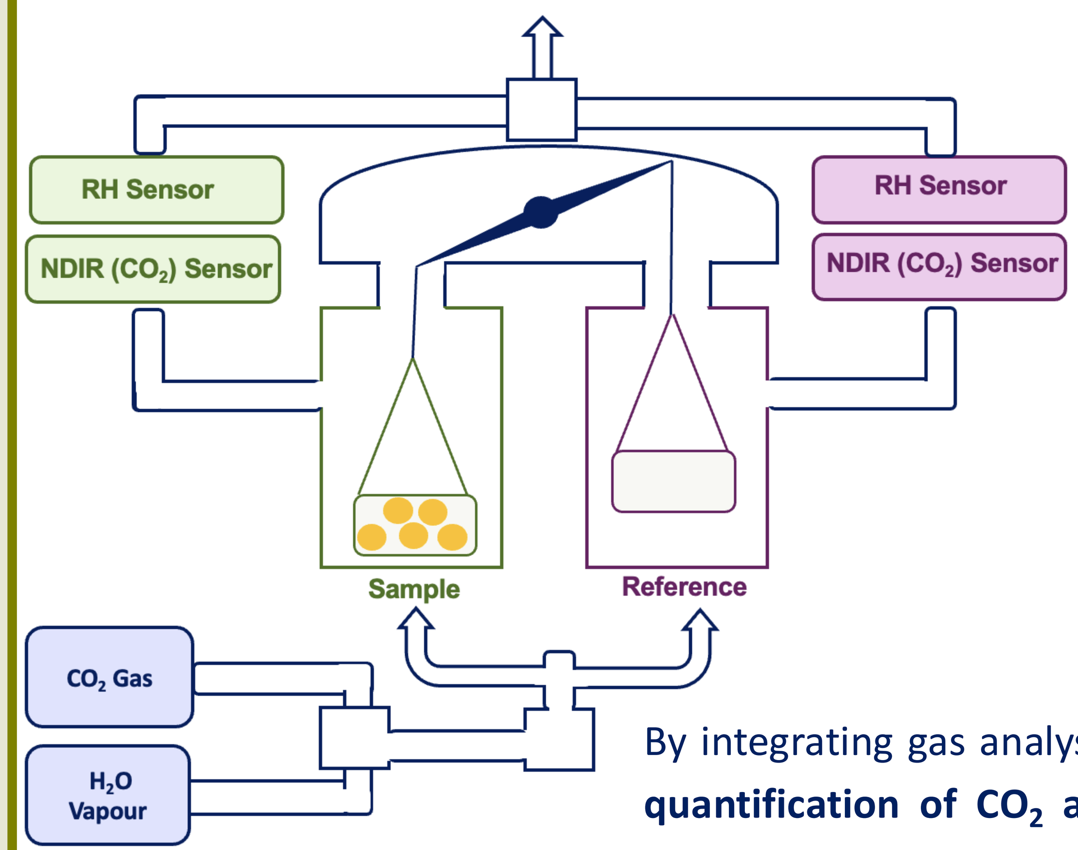
Carbon capture and storage (CCS) is a key strategy for decarbonisation, and solid sorbents such as polymers, zeolites and metal-organic frameworks (MOFs) are one of a suite of promising candidate materials.[1] As such, they require robust characterisation under realistic multicomponent conditions.[2]

Gravimetric methods such as Dynamic Vapour Sorption (DVS) measure the mass change of a sample during adsorption using a microbalance, providing isothermal, time-resolved uptake and equilibrium data. As DVS measures total mass uptake, it reflects combined co-adsorption behaviour and cannot distinguish between co-adsorbed species.[3] As realistic gas steams contains multiple components, including water vapour, a key impurity that can compete for adsorption sites, this limits interpretation of CO_2/ H_2O interactions, typically requiring breakthrough methods to resolve.

CALF-20 is a water-stable MOF widely studied and industrially applied for CO_2 capture in realistic atmospheric conditions due to its high uptake at low concentrations (<20%).[4] It exhibits limited water uptake at low relative humidity (RH), followed by an increased uptake at higher humidity. Under multicomponent conditions, CO_2 and H_2O compete for adsorption sites, and the presence of CO_2 has been shown to suppress water adsorption in low RH.[4] However, this competitive behaviour is difficult to resolve using conventional gravimetric methods.

2 Co-sorption Gravimetry: Integrated Gas Analysis

An integrated system was developed to enable direct measurement of co-adsorption by combining gravimetry with outlet gas composition analysis, and is applied here to investigate co-sorption in CALF-20. The blank chamber contains no sample and provides a reference signal, allowing changes in gas composition due to adsorption to be quantified.

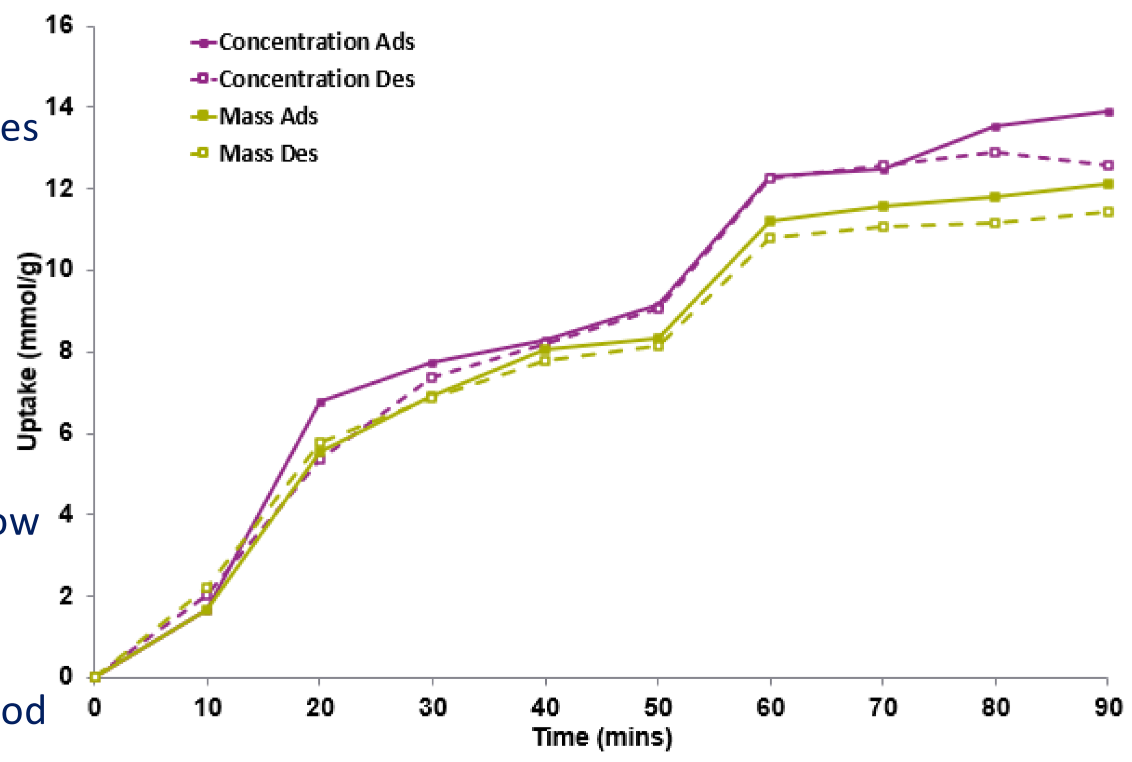


- The UltraBalance (SMS) measures total mass uptake
- NDIR sensors measure CO_2 concentration at the outlets of parallel sample and reference chambers
- RH sensors measure water vapour behaviour at the same locations
- Integrated approach enables symmetrical outflow analysis

By integrating gas analysis, **the system enables simultaneous quantification of CO_2 and H_2O adsorption,** overcoming the limitations associated with traditional gravimetry. In this work, this method is applied to quantify water adsorption and CO_2/H_2O co-sorption in CALF-20.

3 Water Sorption

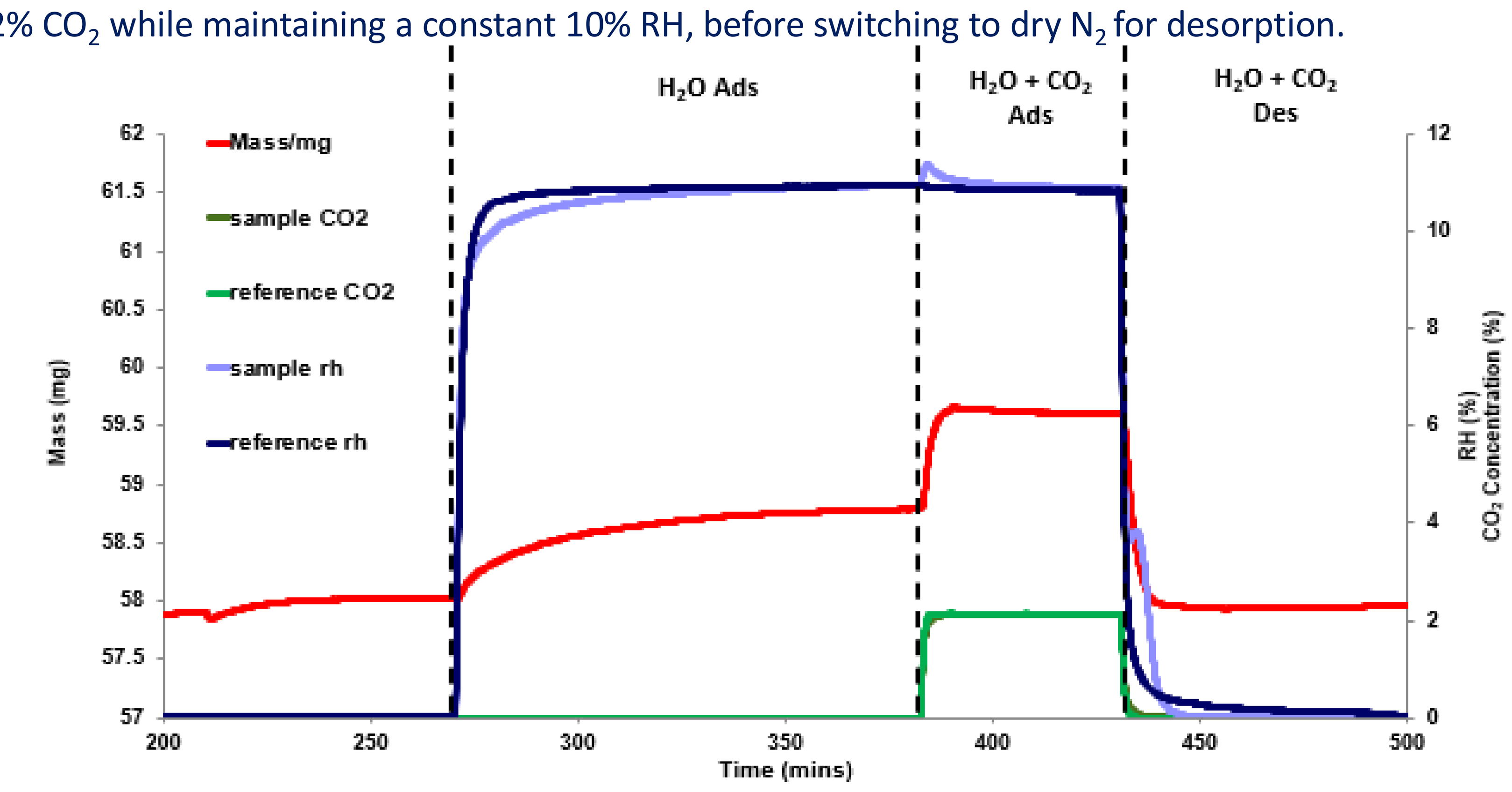
- H_2O uptake on CALF-20 increases with RH, especially above 50% RH, with adsorption and desorption following similar trends
- Uptake calculated from integration of sensor traces show close agreement with DVS measurements across all RH conditions, validating the method



- Measurements were performed at discrete RH steps and referenced to the dry baseline after activation, providing a foundation for future full isotherm experiments

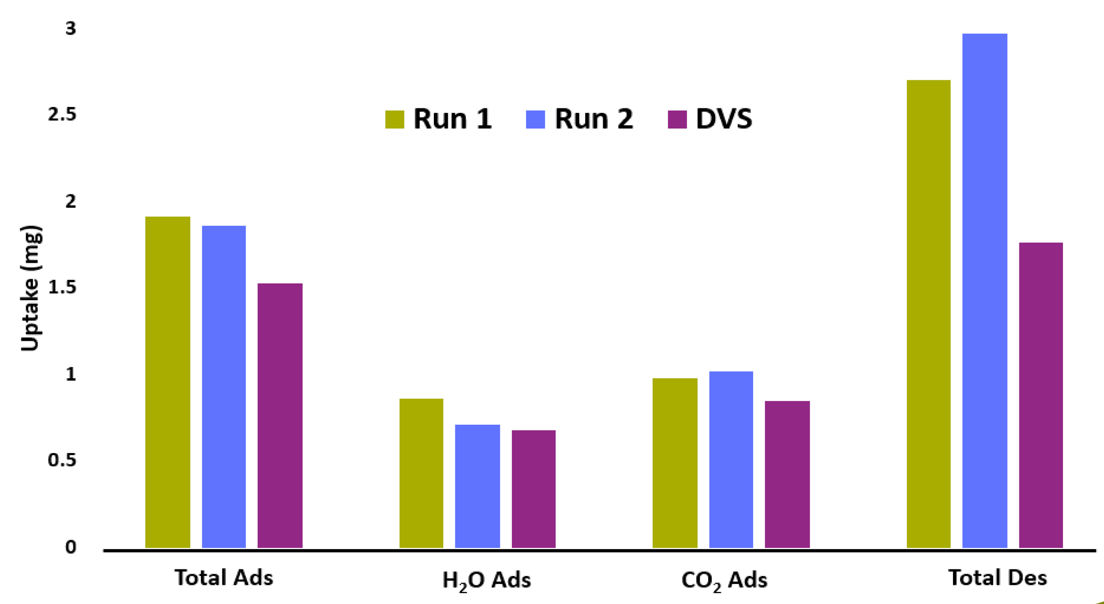
4 CO_2/ H_2O Co-sorption

Experiment: CALF-20 was exposed to 10% RH until equilibrium was reached, followed by introduction of 2% CO_2 while maintaining a constant 10% RH, before switching to dry N_2 for desorption.



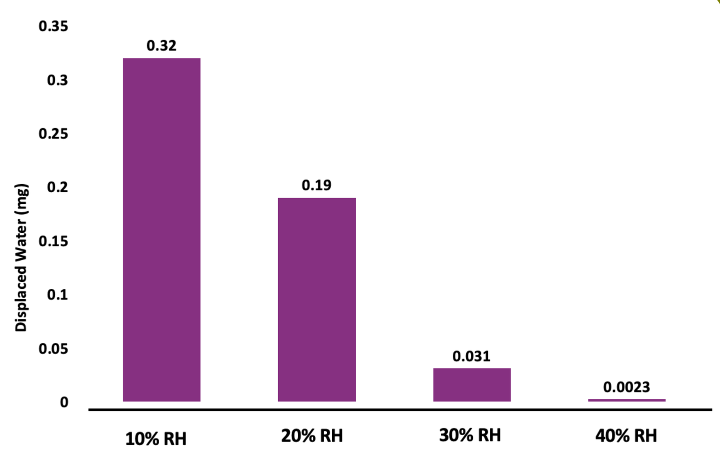
- During H_2O and CO_2 adsorption, the sample signal lags behind the reference while the DVS mass increases, indicating adsorption, these signals can be integrated to quantify the uptake of each gas
- At low RH, the hydrophobic nature of CALF-20 means incoming CO_2 displaces previously adsorbed water, observed as a desorption peak in the sample RH signal [2,4]
- During desorption, removal of CO_2 and RH results in desorption peaks in RH and CO_2 signals and a sharp decrease in DVS mass

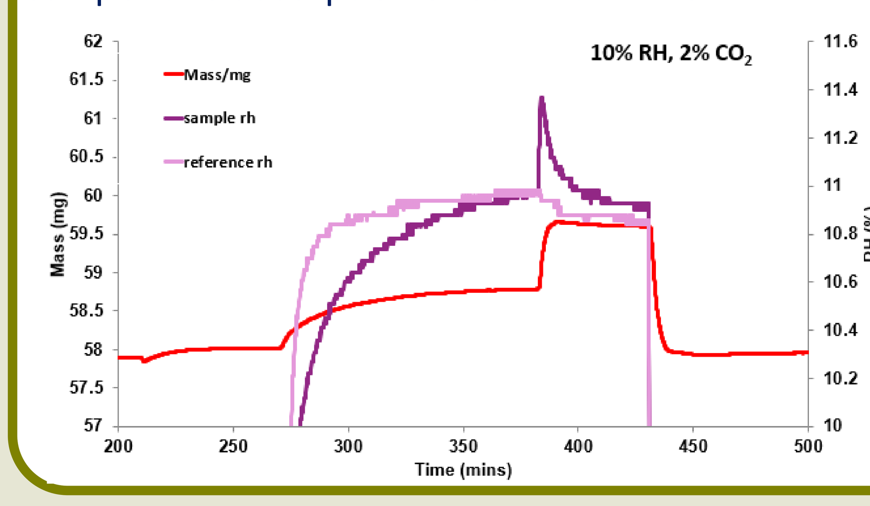
Integrated gas analysis shows strong repeatability and good agreement with DVS measurements, validating the accuracy of the new integrated method.

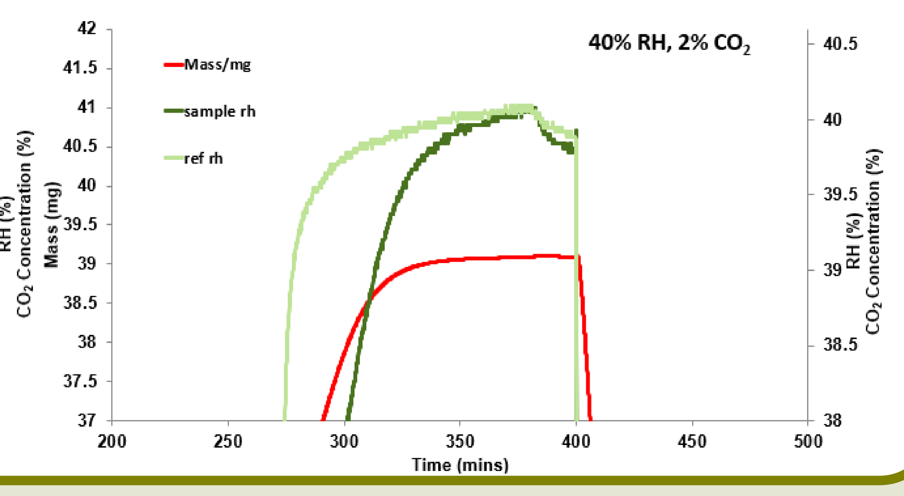


5 H_2O Displacement

Co-sorption experiments were repeated at increasing RH and 2% CO_2. Integrated gas analysis quantifies CO_2-induced displacement of H_2O, showing a clear desorption peak at low RH (10%) that diminishes with increasing RH and becomes negligible at 40%, quantifying a known competitive adsorption effect in CALF-20.[2,4]







6 Conclusions and Future Work

- An integrated gravimetric-gas analysis method enabled independent quantification co-adsorbed of CO_2 and H_2O adsorption in CALF-20, allowing the full two-component co-sorption space to be determined
- Integrated gas analysis shows good agreement with DVS measurements across 0-90% RH, validating the new method
- CO_2-induced water displacement, a known competitive adsorption behaviour of CALF-20, was clearly observed and quantified at low RH (10%) and decreased with increasing RH, becoming negligible at 40%
- In the future other porous materials with applications for carbon capture, including Zeolite 13X and Lewatit will be investigated using this method to further assess multicomponent adsorption behaviour

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