Co-Adsorption of Carbon Dioxide on Zeolite 13X in the Presence of Preloaded Water

Gregory E. Cmarik¹ Jacobs Space Exploration Group, Huntsville, AL, 35812

James C. Knox² NASA/Marshall Space Flight Center, Huntsville, AL, 35812

Environmental Control and Life Support requires highly effective CO₂ removal systems. The current system onboard the International Space Station is known as Carbon Dioxide Removal Assembly. Recent high-fidelity simulation of this system predicted a major efficiency gain via reduction of desiccant zeolite. Commercial beaded 13X zeolite is used in the desiccant bed to scrub water below 1 ppm but is also a highly active CO₂ sorbent. The simultaneous adsorption of water vapor and CO₂ is known to strongly favor water, but more accurate measurements are needed. This work details the characterization of the zeolite to be used in the next-generation CO₂ removal system for co-adsorption of water and CO₂.

Nomenclature

CDRA	=	Carbon Dioxide Removal Assembly
ISS	=	International Space Station
ррт	=	parts per million
MSFC	=	Marshall Space Flight Center
GC	=	Gas Chromatograph/Chromatography
MSB	=	Magnetic Suspension Balance
4BMS	=	4-Bed Molecular Sieve
TGA	=	Thermogravimetric Analysis/Analyzer
MFC	=	Mass Flow Controller
RH	=	Relative Humidity
sccm	=	standard cubic centimeters per minute
STP	=	Standard Temperature and Pressure (0°C, 1atm)

I. Introduction

IN Space Policy Directive-1, NASA's stated goal for the agency is to "advance the nation's space program by increasing science activities near and on the Moon and ultimately returning humans to the surface." Efforts to develop CO₂ removal technologies as part of a closed-loop life support system for these missions are underway. At Marshall Space Flight Center (MSFC), these efforts are focused on producing an International Space Station (ISS) flight demonstration of the next-generation four-bed molecular sieve (4BMS) system. A 4BMS system is a CO₂ removal system which utilizes beds of desiccants and zeolite molecular sieves. This work focuses on the detailed study of the zeolite materials used in this system, where the results will be applied to optimization of the next-generation four-sieves.

Onboard the ISS, one of the systems tasked with removal of the metabolic CO_2 is the Carbon Dioxide Removal Assembly (CDRA). CDRA is a flight-qualified version of 4BMS technology for removal of CO_2 from station cabin air. 4BMS systems use two pairs of sorbent beds packed with desiccant and CO_2 sorbent as shown in Figure 1. The desiccant beds contain a layer of silica gel as the bulk drying material and a layer of 13X zeolite to reduce residual water vapor below 1 ppm. While silica gel adsorbs negligible amounts of CO_2 at the operating conditions, 13X zeolite is a highly active capture medium for both CO_2 and H_2O . An oversized 13X desiccant layer has been found to reduce

¹ECLSS Engineer, Jacobs Space Exploration Group, Marshall Space Flight Center/ES62

²Chemical Engineer, NASA, Marshall Space Flight Center/ES62



Figure 1: Schematic of a 4BMS depicting one half-cycle of operation. Humid cabin air flows through adsorbing desiccant bed (1) and then through a blower and precooler. This cool, dry air passes through a pelletized zeolite sorbent bed (2) where CO_2 is adsorbed and then through desorbing desiccant bed (3). Sorbent bed (2) retains heat from regeneration in the previous half-cycle and this residual heat provides a hot purge to desorb water from the adjacent desiccant bed (3). During this half-cycle, the alternate CO_2 sorbent bed (4) is heated and evacuated to regenerate the sorbent material.

overall system performance by adsorbing CO_2 outside the sorbent beds.¹ A desiccant layer that adsorbs no CO_2 was simulated to improve the time-averaged CO_2 removal rate of the system by 50%. Testing was conducted where the same 13X zeolite desiccant was reduced by half which resulted in a measured 20% increase in performance.² Optimizing the performance of the next-generation 4BMS system is critical to minimizing mass, power, and volume parameters.

The challenge of measuring co-adsorption of CO_2 and H_2O is significant due to the non-linear behavior. Water is adsorbed in significant amounts at concentrations of 1 ppm while CO_2 is adsorbed in similar quantities at 1000ppm concentrations. Additionally, adsorption of small amounts of water vapor causes a significant reduction of CO_2 adsorption capacity, but quantifying the amount of adsorbed water is challenging. Some works have attempted to directly measure the co-adsorption behavior directly³ or indirectly via the behavior of a packed bed.^{4, 5} The material studied here is the commercially available 13X zeolite which is to be used in the next-generation 4BMS system. The initial results for this work were shown in last year's work.⁶ This paper summarizes the efforts conducted to characterize the co-adsorption of CO_2 and H_2O and guide performance optimization of a 4BMS system.

II. Experimental Methods and Procedures

A. Procedures – Rubotherm FlexiDOSE

1. Isotherm measurement via controlled dosing

The primary test instrument is a *FlexiDose MIX FLOW* (G&VLP) unit developed by Rubotherm (now a part of TA Instruments). A photo of the entire system and the Magnetic Suspension Balance (MSB) along with a schematic of the system are shown in Figure 2. This instrument is an automated gas and vapor dosing and mixing system with gravimetric measurement capabilities and an operating range from vacuum to 1.2 bar. Gas mixtures are prepared in an isothermal oven in a control volume which can be circulated internally or across the sample. Measurements are taken in static conditions after stopping the circulation of the gas mixture within the two separated volumes. The sample can be activated at up to 400°C and measurements can be conducted at any temperature from 0°C to 400°C with the heater or fluid jacket. High sensitivity is imparted by the MSB which measures mass changes with microgram accuracy and corrects for ambient fluctuations that occur over the span of a test. A *MasterGC* gas chromatograph



Figure 2: Picture of the system (top left), MSB (right), and a schematic of the system (bottom left) installed at MSFC.

(GC) built by DANI is used to quantify the gas phase concentration of CO₂ and H₂O simultaneously and possesses a sensitivity as low as 0.1% and 0.15%, respectively. The carrier gas used throughout the instrument is helium and total system pressure is maintained at 1 bar \pm 200 mbar during tests. A rotary vane vacuum pump provides vacuum for activation and pressure controllers maintain system pressure at desired levels. A standard procedure has been developed for this unique and complex instrument at MSFC.

2. Calibration

The humidifier is purged with helium at 100 sccm for 2 days to remove dissolved air with periodic sampling via the GC to observe the disappearance of any extraneous peaks. The GC procedure involves an increasing flow and temperature ramp to sharpen and accelerate the elutriation of the components through the column. The final temperature was set to 120° C to ensure the column returns to a dry state. In order to extract a gas sample from the *FlexiDOSE*, Rubotherm built a small sampling volume of the control loop which is isolated via solenoid valves and enables the gas sample to be swept into the GC. Calibration and testing was conducted at only 1 bar as the system pressure was found to significantly affect the GC operation. Sample pressures are normalized to 1 bar when small (<20 mbar) pressure variations are encountered.

In order to further automate the process and minimize the risk of user-induced bias, the GC analysis software was set to use the height of the sample peak to obtain elution mass which is converted via the calibration curve to concentration. The conventional method of integrating peak area to obtained elution mass was determined to be unreliable via both manual calculation and via software automation because of broad peaks. The cause of the broad peaks was the large volume and unswept internal regions of the sampling block, both unavoidable compromises to integrate many valves and sufficient flow capacity. Additionally, large concentrations would lead to partially overlapping peaks. Peak heights were found to be repeatable when all pressures were carefully maintained.



Figure 3: Calibration curves [left] for water and CO₂ obtained for the MasterGC supporting the FlexiDOSE system. Calibration check of mixture versus directly calculated concentration [right] is shown with an X=Y line for visual reference.

Calibration of the GC was determined separately for dry CO_2 and for water vapor. Dry CO_2 calibrations were collected by generating samples manually using the mass flow controllers as well as measuring a 5% CO_2 standard. Water was calibrated by measuring manually generated samples and calculating the expected dew point. The water calibration was found to have an error which was more pronounced at higher flowrates indicating the cause was related to pressure drop. The pressure at the humidifier was measured at each flowrate and incorporated in the calibration. Calibration curves for these two components are shown in Figure 3. A programmed sequence of mixtures of CO_2 and H_2O in helium showed the measurement of each was unaffected by the other in GC measurements. This test did reveal an inherent behavior of the instrument where the CO_2 concentration was consistently below predicted values by about 10%, more so at slower feed rates. The cause was determined to be caused by the transient filling behavior during programmed operation as identical dry CO_2 tests show the same behavior. The original calibration was conducted manually instead of via program thus did not suffer the transient effects and was accurate.

Approximately 350mg of sample is used for each test which corresponds to roughly a single layer in the sample basket. A thin sample minimizes the risk of non-uniform adsorption. Once a sample is loaded, it will be tested up to 20 times. Leak checks are conducted by running a blank test. Leak tightness is determined by inspecting the raw test data which easily reveals if a leak is occurring at vacuum and for an initial pressure of 1.2 bar. Prior to each isotherm, the sample is pretreated (activated) via heating to 350° C with alternating 30 minute vacuum and helium purges. The sample is soaked at 350° C for 4 hours under vacuum then a helium purge. At least one CO₂ isotherm is conducted without water preloading for comparison to dry reference data.

4. Sample Preloading with Water Vapor

Co-adsorption measurements are conducted by preloading the sample with water. Preloading involves flowing helium through a humidifier then over the sample for a set number of minutes. This is an open loop flow thus at the end of the step there remains some humid gas in the upstream tubing, a fact which became apparent after a small number of tests. Future tests included a step in the automation to ensure the preloading was completed. As all preloadings were conducted at the same dew point, a single correction can be applied to all tests which was found to be 0.15-0.20 mol/kg (varies slightly with actual sample mass). The mass change over this time is assumed to be due to water adsorption and provides the water preloading for the isotherm and is assumed to remain constant for the remainder of the measurement.

Control tests at 25° C have shown no detectable water in the circulating loop after any measurement points which indicates that water remains adsorbed even though dry gas is circulated across the sample for the remainder of the test. This was used to justify the assumption that preloaded water does not desorb in significant quantities thus enabling a direct CO₂ isotherm measurement. Eventually, a test with a large enough preloading of water was attempted where traces of water were observed in the dry gas circulation indicating a limit to the available testing envelope. Higher temperatures were treated in the same manner and the maximum water vapor preloading was smaller as temperature rose. This observation is in line with expectations.

5. Preloaded Isotherm Measurement

A preloaded CO_2 isotherm is produced by generating mixtures of dry CO_2 in helium then circulating the mixture across the sample. Prior to measuring each isotherm point, the control loop is evacuated then refilled via the MFCs. After a few minutes, the control loop is sealed and a sample is swept out of the sampling block to be measured with the GC. The prepared gas within the loop is circulated across the test sample. After approximately one hour (longer when larger mass increases are expected), the circulation is stopped, the control volume is isolated, and a gas sample is taken to obtain the concentrations after each point. The resulting isotherm is calculated from the combined mass change data and GC data.

As the range of preloadings and temperatures was expanded, the assumption of no water desorption was found to eventually become invalid. Since this procedure depends on the assumption that preloaded water does not significantly desorb, the test range of temperature and water preloading became bracketed. The tests reported here were conducted at 25, 50, 75, and 100°C.

B. Procedures - SETARAM Sensys Evo

1. Isotherm measurement

Another instrument with similar capabilities is the SETARAM *Sensys Evo* Thermogravimetric Analyzer (TGA) with the *Wetsys* humidity generator option. In addition to the *Wetsys*, the system was further modified with an MFC which supplies supplementary dry N_2 and a LICOR *LI-840a* CO₂/H₂O gas analyzer. On occasion, an Edgetech *DewMaster* chilled mirror was used for water vapor calibrations.

Gas mixtures can be generated with a control of composition of H_2O and CO_2 with a N_2 carrier. As an approximation, N_2 was considered to be a non-competing carrier gas for these tests. Put into practice, this means that the desorption of N_2 due to competition from H_2O and/or CO_2 would be an insignificant mass change. A practical maximum flowrate of 150 sccm was found to exist, as higher flowrates would lead to noisy behavior. This resulted in a small range of achievable concentrations which still included enough range to validate the data obtained from the Rubotherm instrument but not enough to stand alone for modelling purposes. The results of these co-adsorption measurements were therefore only used to validate results.

Due to the low concentrations of water vapor and low flowrates, equilibration requires a long time. Small samples were used to compress test times to the span of days but this revealed a couple limitations of the system. First, significant water adsorption occurred even at extremely low concentrations which were difficult to accurately measure. Second, the small mass change due to the small sample size could be obscured by thermal fluctuations in the lab affecting the microbalance which was not thermostatted. Third, the water vapor concentration of the inlet could not be set to zero without manually disconnecting the *Wetsys*.

2. Calibration

The TGA balance is tared at the start of every test at stagnant conditions. To ensure equal drag forces across the sample and reference pans the flowrate is set to test conditions. The flow splits in the tubing internal to the TGA, thus the split flows are adjusted until the balance again reads zero. The *LI-840a* was calibrated first with dry nitrogen to zero the optical sensor for water and CO₂. Second, a dew point of roughly 5°C in N₂ was generated, flow was diverted though and measured in an Edgetech *DewMaster* chilled mirror sensor to obtain the span for H₂O vapor. Finally, CO₂ was calibrated against a calibration standard of 5,000 ppm in N₂. A schematic of the integrated system is provided in Figure 4.



Figure 4: Schematic of integrated Sensys Evo TGA, *Wetsys*, additional MFC, LI-840a, and DewMaster.

3. Sample Preparation

Samples are loaded via manual selection of ~7 beads of Grace-Davison MS544 13X zeolite which are placed into the sample basket targeting 50mg while the reference basket remains empty. Since the basket is narrow, the beads are well exposed to the air flow even if the basket is filled with several layers. Sample activation is included in the entire test schedule as design in the software and includes a constant purge of N_2 as the sample heats at 5°C/min to 350°C then soaked for 4 hours before finally cooling at 10°C/min to test temperatures. The mass change observed during cool down has been correlated to N_2 isotherms reported in literature⁷ with good agreement. The mass of the sample

measured just before cool down begins while the temperature is at its maximum and is used as the dry mass for later adsorption calculations.

4. Sample Preloading with Water Vapor

Samples are loaded with water vapor at the test temperature via mixing of a humidity controlled output from the *Wetsys* and supplemental dry gas from the MFC. Preloading is completed after 30 minutes where the *Wetsys* is programmed to switch back to 0% relative humidity (RH). Due to adsorption of water within the long transfer lines and extra system volumes, the switch does not instantly reduce water vapor concentrations in the gas flow to zero, thus a curve subtraction method was implemented.

The curve subtraction method involves fitting a line to the residual mass increase over a long time after water flow is set to zero in the programming. This 'blank' is later used as a subtraction to determine mass changes due only to CO₂. This method effectively bypasses the three previously described systematic errors.

5. Preloaded Isotherm Measurement

Segments for isotherm measurement are conducted in pairs: the first portion activates the sample at up to 350° C while the second obtains a single data point for H₂O/CO₂ co-adsorption. The adsorption step first preloads the sample with water, then after water flow in the *Wetsys* was set to 0% RH, CO₂ flow is turned on. The mass change associated with CO₂ uptake was the remainder when the blank segment is subtracted. After subtraction, the maximum mass is used as the quantity of CO₂ adsorbed and the mass subtracted at that time during the blank measurement is used to determine water adsorption.

III. Results and Discussion

A. CO₂ Isotherms Obtained at Various H₂O Preloading

The results obtained with the *FlexiDOSE* at 25°C are shown in Figure 5 along with reference isotherms of both dry, pure component CO_2 measurements^{8,9} and a set of similar water preloaded measurements.³ The pure component CO_2 isotherm is measured from extremely low vacuum with only CO_2 whereas all of the preloaded isotherms are CO_2 in a Helium carrier. The pure component CO_2 isotherm and the measurements presented here were on the same lot of MS544 13X zeolite. When plotted in a log-log format, the Henry's law behavior occurs at low CO_2 partial pressures and should be visible as a 45° linear segment, but some of the isotherms measured here deviate to slightly steeper lines which suggest incomplete equilibration. To minimize this issue, longer circulation times in the program were used when conditions enable larger quantities of CO_2 to be adsorbed.

The first comparison to be made is between the zero preloading tests and the reference isotherm⁸ which shows the new data to be slightly imperfect. The low pressure data deviates below expected Henry's law behavior and the entire isotherm appears to have an offset of roughly 0.2 mol CO_2/kg across the pressure range. The second comparison is between preloaded tests from this work and from the reference data³ where a significant difference is observed. The authors of that work noted the low activation temperature of 175°C which could be achieved in their system would



Figure 5: CO₂ isotherms measured on MS544 13X at a number of water preloadings in the FlexiDOSE system. *Reference data.⁸ **Reference data.³



Figure 6: CO₂ isotherms measured on MS544 13X at a number of water preloadings in the FlexiDOSE system. *Reference data.⁸ **Reference data.³

likely have an effect on test results. Comparing the closest isotherms it appears that roughly 1.5 mol/kg of water was not desorbed at 175° C in their tests and thus remained unaccounted for in the preloading determination.

Further isotherms were gathered at 50°C and 75°C as shown in Figure 6 along with the reference isotherms available.³ The preloading difference versus published values for the 50°C measurements appears to be roughly 1.0 mol/kg. Some 75°C isotherms were observed to cross which would be an unrealistic phenomenon when only physisorption mechanisms are considered. This measurement error has not yet been resolved and the small data set does not allow for exclusion of data. Fortunately, the errors do appear to be small and only affect data points at very low CO_2 partial pressures indicating that the error is with the method and instrument.

Further isotherms were gathered at 100°C as shown in Figure 7 but, at this temperature, the assumption of invariant water preloading began to break down. Traces of water vapor were detected by the GC in the gas samples throughout this test series indicating slow desorption with each step of the measurement. Higher mass uptake was observed for preloaded samples than is measured for dry sorbent at low CO_2 partial pressures. At this time, no satisfactory cause has been identified for this behavior. If water was desorbing in significant amounts, the mass change and thus calculated capacity of each point would be decreased whereas here the calculated capacity is increased above dry isotherm conditions. Isotherms were measured at 175°C as well, but significant desorption of water during each step at low water preloading invalidates the assumptions for this test series.



Figure 7: CO₂ isotherms measured on MS544 13X at a number of water preloadings in the FlexiDOSE system. *Reference data.⁸

B. Mixture isotherm model

The next step taken with the raw data was to fit an isotherm model in Excel. Utilizing the isotherm model developed previously for pure component CO2 with isotherms measured at Ames Research Center and Marshall Space Flight Center⁹ as a basis, a number of simple modifications were trialed. The primary assumption for these modifications is that water adsorption is unaffected by the adsorption of CO₂ and that water adsorption in a dynamic system is rapid and irreversible at low temperatures. In the dynamic system described earlier, the model of the desiccant bed of CDRA, CO₂ is adsorbed to equilibrium in the mostly-dry 13X layer while¹ the silica gel layer is adsorbing all incoming water vapor. The traces of water vapor which break through the silica gel layer are immediately adsorbed on the 13X layer and some amount of CO₂ is desorbed to return to the new equilibrium.

The first modification was to apply a linear relationship between loading and capacity loss which is shown in equations 1-4. The water preload was multiplied by a fitting factor, *f*, to yield a CO₂ capacity modifier. This model predicted that CO₂ adsorption, n_{CO2} , would be zero when water loadings, n_{H_2O} , exceed 3.6 mol H₂O/kg. This fitting parameter, $n_{H_2O}^*$, was obtained by fitting the existing isotherm data at preloadings below 2.5 mol H₂O/kg.

$$f_{H_20} = \frac{n_{H_20}}{n_{H_20}^*} \tag{1}$$

(2)

(3)

(6)

and

where,

$$n_{H_20}^* = 3.6 \, mol \, H_2 O / kg$$

and where,
$$n_{CO_2}^* = \sum_{i=1}^3 n_{sat,i} * \frac{b_i * P_{CO_2}}{(1 + b_i * P_{CO_2})}$$
(4)

 $n_{CO_2} = n^*_{CO_2} * (1 - f_{H_2O})$

As preloadings greater than 2.5 mol H_2O/kg were measured, it became apparent that the relationship between water preloading and CO₂ capacity loss was not linear. A two parameter fitting equation was designed of the form of the familiar Toth isotherm¹⁰ where pressure is replaced by water preload and the parameters 'b' and 't' are fitting parameters. This model is entirely empirical and no attempt to derive from basic theory has been conducted at this time. Also, the model has no temperature dependence beyond the previous dry CO₂ adsorption model. The resulting two component model is shown in equations 5-6.

$$f_{H_2O} = \frac{b_{H_2O} * n_{H_2O}}{\left(1 + \left(b_{H_2O} * n_{H_2O}\right)^{t_{H_2O}}\right)^{1/t_{H_2O}}}$$
(5)

and

$$h_{CO_2} - h_{CO_2} * (1 - J_{H_2O}) \tag{0}$$

The results of fitting this model to the data for 25° C are shown in Figure 8. The results are promising. A good fit is observed at the future partial pressure of CO₂ onboard crewed missions of 0.26 kPa. Table 1 lists the parameters of the proposed best-fit model.

A more focused comparison is shown in Figure 9. To generate this plot, a single value was calculated from the model to match the isotherms at a desired pressure and compared to a single measured value interpolated for each isotherm. A CO₂ partial pressure of 2 kPa



some conditions. In addition, the values were normalized to the measured dry value to observe whether the effects of water are consistent across temperatures. The normalized values for the 100°C isotherm were excluded due to the small absolute values.

was chosen as this was observed to be a

measured point for interpolation at all

temperatures and preloadings. Generating

this plot at 0.5 kPa or lower was not

possible as points were not obtained for

 Table 1: Best-fit parameters for discussed

 two-component isotherm models.

 Fitting

Fitting		
Parameter	Value	Units
$n_{H_{2}0}^{*}$	3.6	mol H ₂ O/kg
$b_{H_{2}0}$	0.500	(mol H ₂ O/kg) ⁻¹
t_{H_20}	1.251	[-]

Figure 8: Result of proposed model fit to data obtained at 25°C.



Figure 9: Visualization of model-data agreement on absolute and normalized scales. Comparison shows a single pressure point for each measured isotherm.

C. Validation of measurements

The measurements to this point that have been conducted with the *FlexiDOSE* system show disagreement with reference data¹⁰ and are not yet validated with a second instrument at MSFC. The validations were conducted at a few discrete points with a SETARAM *Sensys Evo* TGA with the comparisons shown in Figure 10. The results fail to show excellent agreement and suggest a smaller sensitivity to water vapor than as measured in the *FlexiDOSE*. In fact, the results from the TGA would suggest the reference data³ contained a significantly larger preloading error than the previously determined 1.5 mol/kg.

One possible cause of this discrepancy is that the sample size of ~50mg was too large for this system despite being a small fraction of the sample size in the *FlexiDOSE*. In this system, a wire mesh basket is suspended in a gas flow with the top and sides exposed to the mixture. All beads of the sample are wholly visible from multiple angles through the sides of the wire basket but not in the direction of flow where the beads are stacked several layers deep. The adsorption behavior for water onto 13X is rapid with a high capacity while the gas flow delivering the water vapor is slow. Perhaps only the topmost layer of beads were exposed to water vapor and adsorbed all traces, leaving the lower layers dry despite direct contact with the gas flow. The proposed adsorption model indicates that the first traces of water adsorption have the greatest effect, so an evenly distributed preloading would show a greater reduction of CO_2



Figure 10: CO₂ isotherms measured on MS544 13X at a number of water preloadings in the SETARAM TGA. *Reference data.⁸ **Reference data.³ γ *FlexiDOSE* data.

adsorption versus a layered sample showing equal mass change. Future testing would need to develop a new test plan to accommodate for this behavior.

IV. Conclusions

This work details a series of efforts to characterize the co-adsorption of water vapor and carbon dioxide on Grace-Davison MS544 13X zeolite which is in use onboard the ISS and slated for use in the next-generation 4BMS system. Detailed measurement methods are provided to aid future efforts in measurement of this highly non-linear system.

The effect of water adsorption on 13X zeolite is pronounced and can have a substantial impact on overall system performance. This 13X zeolite is used in both the desiccant and CO_2 removal beds of the next-generation 4BMS system, further increasing the importance of accurate inputs for computer simulation. The 13X layer of the desiccant bed is exposed to both water vapor and CO_2 during every cycle and optimizing this layer can improve the system performance. The 13X in the CO_2 removal beds remains very dry but well-measured contingencies improve the reliability of the system.

This work provides direct measurements and a model for use in a detailed system simulation. The data indicates that CO_2 adsorption drops rapidly with the adsorption of a small amount of water. For example, half of the CO_2 capacity of dry 13X is lost when 1.25 mol/kg of water is adsorbed. The equation proposed to fit the two-component measurements is similar to the Toth isotherm with water loading replacing partial pressure. Previously measured isotherms for dry sorbent are used as the basis of this model and the effect of water loading is introduced as a prefactor. Further work is recommended to refine the measurements and develop a more accurate model.

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