Investigation of Desiccants and CO_2 Sorbents for Exploration Systems 2016-2017

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NASA has embarked on the mission to enable humans to explore deep space, including the goal of sending humans to Mars. This journey will require significant developments in a wide range of technical areas as resupply and early return are not possible. Additionally, mass, power, and volume must be minimized for all phases to maximize propulsion availability. Among the critical areas identified for development are life support systems, which will require increases in reliability as well as reduce resource usage. Two primary points for reliability are the mechanical stability of sorbent pellets and recovery of CO_2 sorbent productivity after off-nominal events. In this paper, we discuss the present efforts towards screening and characterizing commercially-available sorbents for extended operation in desiccant and CO_2 removal beds. With minimized dusting as the primary criteria, a commercial 13X zeolite was selected and tested for performance and risk.

Nomenclature

4-BMS	=	Four-Bed Molecular Sieve
ARC	=	Ames Research Center
ASTM	=	American Society for Testing and Materials
CDRA	=	Carbon Dioxide Removal Assembly
HST	=	Hydrothermal Stability Test
ISS	=	International Space Station
LSS	=	Life Support Systems
NASA	=	National Aeronautics and Space Administration
MSFC	=	Marshall Space Flight Center
TGA	=	Thermogravimetric Analysis
TC	=	Thermocouple
mmHg	=	millimeter of mercury (Torr)
slpm	=	standard liters per minute (STP = 0°C, 760 mmHg)
LiLSX	=	Lithium, Low-Silica X-type Zeolite

I. Introduction

IN "NASA's Journey to Mars: Pioneering Next Steps in Space Exploration"[1] the stated goal for the agency is to *"extend human presence deeper into the solar system and to the surface of Mars."* As also stated therein, *"It is time for the next steps, and the agency is actively developing the capabilities that will enable humans to thrive beyond Earth for extended periods of time, leading to a sustainable presence in deep space."* The three phases required to reach these goals are defined as "Earth Reliant", "Proving Ground", and "Earth Independent." In the first and current phase, *"**Earth Reliant** exploration is focused on research aboard the International Space Station (ISS). On the space*

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station, we are testing technologies and advancing human health and performance research that will enable deep-space, long-duration missions." One of those technologies listed is *"Mars mission class environmental control and life support systems."* Efforts to develop CO_2 removal technologies as part of a closed-loop life support system for Exploration missions are underway. These efforts are focused on producing ISS flight demonstrations of a CO_2 removal system which utilizes beds of desiccants and molecular sieves and is known as four-bed molecular sieve (4-BMS). This work focuses on the study and selection of these materials, where the results will be applied to design future 4-BMS systems for exploration missions and to improve the system in use onboard the ISS.

In order to enable a 4-person crew to successfully reach and return from Mars or other deep space location, systems for removal of metabolic carbon dioxide must reliably operate for several years while minimizing power, mass, and volume requirements. This minimization can be achieved through system redesign and/or changes to the separation material(s). A screening process is required to make the best material selection for a future closed-loop carbon dioxide removal system. The screening process will retain the most reliable material(s) and provide the information necessary to guide system design via sorbent characterization.

On board the ISS, one of the systems tasked with removal of the metabolic carbon dioxide is a specialized 4-BMS known as CDRA. A schematic of a 4-BMS system is shown in Figure 1. The materials used in the desiccant beds are layers of silica gels and 13X zeolite which reduce inlet dew points to -90°C or lower while CO_2 removal beds contain pelletized 5A zeolites. The present CDRA system maintains a cabin CO_2 concentration of 3.5 torr on the ISS but new requirements seek to reduce this to 2 torr to improve crew health and mission effectiveness.[2-4] This reduced concentration leads to increased power requirements and reduced operating lifespan of CDRA. Also, the current CO_2 sorbent, ASRT, can no longer be produced which necessitates the selection of an alternative CO_2 sorbent for CDRA. The search for robust materials with improved properties for the long-term, cyclic operation of CDRA and of an exploration 4-BMS system is the focus of this work.
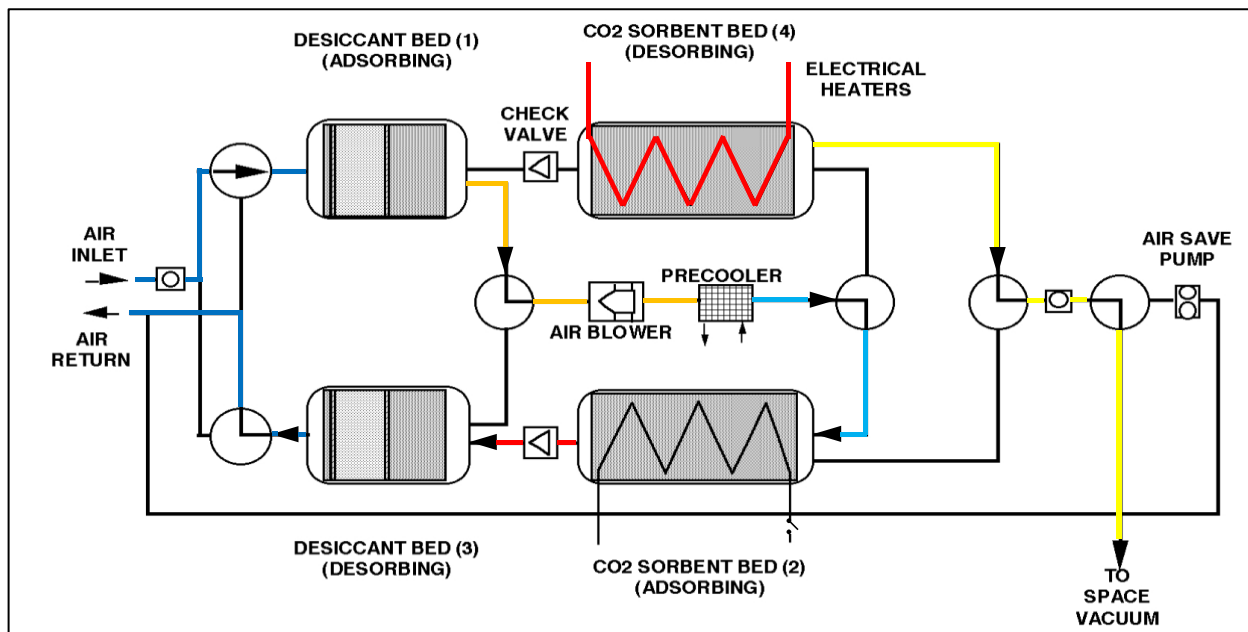
Figure 1. Schematic of a 4-BMS depicting one half-cycle of operation. Humid cabin air flows through adsorbing desiccant bed (1) and then through a blower and precooler. This cool, dry air passes through a pelletized zeolite sorbent bed (2) where CO_2 is adsorbed and then through desorbing desiccant bed (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.

The desiccant beds are composed of multiple layers: guard, bulk removal, and residual removal. The guard layer consists of a robust material at the front of the bed which captures any entrained liquid water droplets (misting). The bulk desiccation layer consists of a microporous silica gel which captures a majority of incoming water vapor. The residual desiccation layer consists of a pelletized zeolite with high water affinity and fast kinetics in order to adsorb

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all measurable traces of water. The CO_2 removal beds in the current CDRA configuration are uniform packed beds of 5A zeolite with an embedded heating element with a design operating temperature of 400°F (204°C).

The works by Watson, et.al.[5] and Knox, et.al.[6] describe the recent efforts for downselecting from many commercially available materials. The predecessor[6] to this work describes the selection of guard and bulk desiccants but only partially covered the residual desiccant and CO_2 sorbent selections. Table 1 lists the factors considered in downselecting from the wide array of beads and pellets and is a simplification of the sorbent performance factors table from the work by Knox.[7] Initial screening with sample quantities of each material involves tests which only consume small quantities of material and allow elimination of some sorbent candidates. Remaining candidates are procured in larger quantities which allows for more detailed and representative characterization tests. Some time-intensive tests are conducted on only the prime candidates such as tests with a programmable Thermogravimetric Analysis (TGA) instrument or purpose-built test stands such as the Hydrothermal Stability Test (HST) stand.[8]

Table 1. Sorbent Screening Performance Factors

Intrinsic Performance Factors	Screening Criteria	Simulation Input	Extrinsic/Pellet Performance Factors	Screening Criteria	Simulation Input
Single Gas Equilibrium Capacity	✓	✓	Single Pellet Crush Strength	✓	
Heat of Adsorption	✓	✓	Bulk Crush Strength	✓	
Adsorption Kinetics	✓	✓	Pellet Friability	✓	
Moisture Sensitivity	✓		Thermal/Hydrothermal Stability	✓	
Cyclic Working Capacity	✓		Packing Density/ Pressure Drop	✓	✓

Detailed study of these materials involves measuring samples in laboratory environments which closely simulate conditions in the 4-BMS system as well as predicting long-term reliability. The adsorption test results are used as inputs for a detailed simulation of the 4-BMS system as described by Coker.[9] The structural performance tests are used to compare the materials amongst themselves and as a filtering metric to remove materials that show traits which may critically impair system reliability.

The structural tests are approximations of the performance of the materials after exposure to high temperatures, moisture, and mechanical forces. The work by Waston[5] provides detailed method development and procedures for measuring the structural properties of the materials in this study and details of those efforts up to the previous publication.[6] The work by Miller[8] details the design and initial use of a specialized test stand to study the stability of parallel packed beds of test material over thousands of hours of thermal cycling in the absence and presence of trace water vapor. The full results of those two efforts are summarized in this work. The five candidate CO_2 sorbents closely considered between the 2016 and 2017 downselects were: Grade 522 5A, Grade 544 13X, BASF 13X, APGIII 13X, and VSA-10 LiLSX. Table 2 provides the materials we have tested for applications in past and future 4-BMS systems. Some materials have been tested more thoroughly than others due to the downselect events and testing availability.

The critical parameter for future systems has been determined to be propensity to generate dust during operation. Dust can critically impair the operation of moving parts and seals within a 4-BMS system or damage other systems such as pumps and compressors. Additionally, larger dust particles which are captured upon filter media lead to flow restrictions. Choked flow leads to increased system pressure drop which eventually overwhelms the system air blower capacity and necessitates system shutdown and maintenance. In the past, dust from RK-38 has caused screen blinding in only 6 months and dust from ASRT has caused various failures over several years and system iterations. Minimizing dust generation has emerged as the primary selection criteria and this work will discuss the sorbent selections made with a keen focus on that property.

Table 2. Materials used in CDRA and/or Included in the Sorbent Screening Study 2016-2017

Material Type	Sorbent Name	Use/Potential Use	Form Factor	Pore size	Notes
Silica Gel	Grace Grade 40	Bulk Desiccant	Granular	Microporous	used in CDRA
Silica Gel	Grace SG B125	Bulk Desiccant	Beads	Microporous	used in CDRA
Silica Gel	BASF Sorbead H	Bulk Desiccant	Beads	Microporous	
Silica Gel	BASF Sorbead R	Bulk Desiccant	Beads	Microporous	
Alumino-Silica Gel	BASF Sorbead WS	Guard Layer	Beads	Microporous	Misting Stable, used in CDRA
Activated Alumina	BASF F200	Bulk Desiccant	Beads	Mesoporous	Misting Stable
Molecular Sieve	UOP ASRT 1995 and ASRT 2005	CO_2 sorbent	Pellets	5Å	CaA Zeolite, used in CDRA
Molecular Sieve	UOP RK-38	CO_2 sorbent	Beads	5Å	CaA Zeolite, used in CDRA
Molecular Sieve	Grace MS 564	Residual Desiccant	Beads	3Å	KA Zeolite
Molecular Sieve	Grace MS 514	Residual Desiccant	Beads	4Å	NaA Zeolite
Molecular Sieve	UOP UI-94	Residual Desiccant	Pellets	4Å	NaA Zeolite
Molecular Sieve	Grace MS 522	CO_2 sorbent	Beads	5Å	CaA Zeolite
Molecular Sieve	Grace MS 544	CO_2 sorbent, Residual Desiccant	Beads	10Å	NaX Zeolite, used in CDRA
Molecular Sieve	BASF 5A	CO_2 sorbent	Beads	5Å	CaA Zeolite
Molecular Sieve	BASF 5A BF	CO_2 sorbent	Binder-free Beads	5Å	CaA Zeolite
Molecular Sieve	BASF 13X	CO_2 sorbent, Residual Desiccant	Beads	10Å	NaX Zeolite
Molecular Sieve	BASF 13X BF	CO_2 sorbent	Binder-free Beads	10Å	NaX Zeolite
Molecular Sieve	UOP APGIII	CO_2 sorbent	Beads	10Å	NaX Zeolite
Molecular Sieve	UOP VSA-10	CO_2 sorbent	Beads	10Å	LiLSX Zeolite
Molecular Sieve	Tosoh NSA-700	CO_2 sorbent	Pellets	10Å	LiLSX Zeolite

II.   Experimental Methods and Procedures

A. Structural Test Procedures

The structural test procedures are based on their respective ASTM methods and adapted to enable humidity conditioned testing. These tests are referred to here as single pellet crush, bulk pellet crush, and attrition. Details on methods for determining the pellet structural properties listed in this work can be found in the works by Knox[7] and Watson.[10] Additionally, the work by Watson details the augmented methods developed to test structural properties for materials under controlled humidity conditions. The data obtained in the single pellet crush test include the mean and variance among crush strengths for the 3 sets of 50 pellet test lots. Also, during the crush of each pellet, dusting can occur which is the release of fine particles prior to the ultimate crush strength. The fraction of pellets in each test lot which dust and the mean force applied to initiate dusting are also recorded.

The Hydrothermal Stability Test (HST) stand[8] is designed to expose a small-scale sorbent bed to hundreds of temperature cycles under a N_2 stream with a controllable dew point over a period of months. The HST was designed in response to evidence of water entering the CO_2 sorbent beds on station which was correlated to a rapid increase in pressure drop across the CO_2 sorbent beds packed with RK-38. The tests measure increases in pressure drop over time for candidate sorbents which is the directly observable result of sorbent breakdown in a packed bed configuration. This test provides strong evidence for and is considered to be highly predictive of the stability of materials over long-term operation.

B. Adsorption Test Procedures

Candidate CO_2 sorbents are tested for pure component adsorption of CO_2 from vacuum to 1 atm in several instruments: a Micromeritics ASAP 2020, a Quantachrome Autosorb-1C and a Quantachrome Autosorb-1. The ASAP 2020 is located at Ames Research Center (ARC) while the two Autosorb instruments are at Marshall Space Flight Center (MSFC). The critical parameter to testing with each of these systems falls to sample preparation, particularly the complete exclusion of atmospheric moisture after sample activation up to 350°C. This exclusion is achieved by activating samples in the testing port of the system, thereby avoiding any exposure during transfer between ports. In all of the tests for CO_2 adsorption, bottled N_2 (99.999%) and CO_2 (99.99%) were used. In order to exclude all traces of ambient moisture from the dry gases, all-metal tubing was used and flexible hoses were avoided.

The Humidity Conditioning Stand (HCS) is designed to provide a constant supply of low dew point N_2 to six ports in parallel. This system has high accuracy dew point sensors and achieves dew point control by mixing dry N_2 with a small amount of humidified gas controlled via a feedback control loop. Due to the extremely low quantity of water vapor supplied to each port, breakthrough experiments can be conducted as the breakthrough time is much longer than other transient effects. The simplicity of this test stand prevents precise fitting of a model, but equilibrium capacity and comparative adsorption kinetics can be determined. In preparation for testing, samples are dried in ovens under a dry N_2 purge, then transferred to a glove box. Test cells are packed in a glove box and sealed prior to transfer to the test stand.

The Cylindrical Breakthrough (CBT) test stand at MSFC is used to precisely measure the behavior of dynamic adsorption in a bench-scale packed bed of roughly 100g. Measurements available to the CBT test stand include bed pressure, differential pressure, temperature profile at the centerline and at the container exterior, sampling of gas concentrations at the inlet, outlet, and within the sorbent bed, and control of CO_2 and/or water vapor concentration in up to 20 SLPM dry N_2. Centerline sampling from within the packed bed occurs roughly 2 pellet diameters above the baseplate supporting the bed while measurement of the bulk flow occurs far from the bed to ensure complete mixing. Measurement of this centerline sampling flow has been conducted with a MicroGC 3000 for dry CO_2 testing, and later with a LICOR Li840a for either dry CO_2 or water vapor testing. The results from this test provide the high fidelity data for (1) derivation of mass transfer coefficients and (2) validation of computer simulations which enables predictive scale-up to full-sized systems.

A custom gravimetric adsorption instrument produced by Rubotherm was designed and built for the purpose of extremely precise and well-controlled adsorption measurements involving both water and CO_2. Once loaded, the sample can be activated at vacuum and up to 350°C, then tested at any temperature down to 10°C. The water preloaded CO_2 isotherms which are obtained with this instrument are measured by a Rubotherm microbalance for mass uptake and a Dani MasterGC for gas phase concentration of water and/or CO_2 in a helium carrier. Prior to each isotherm, samples are fully activated up to 350°C. At least one isotherm is conducted without water preloading for comparison to dry reference data. Preloading of water involves flowing 100 sccm of helium through a humidifier then over the sample for a set number of minutes. A CO_2 isotherm is produced from circulating a measured mixture of CO_2 in helium across the sample within a loop. The resulting isotherm covers a measurement range from 0.1 up to a maximum

of 6.0 kPa CO_2. Control tests have shown no detectable water in the circulating loop after any measurement points which indicates that water remains adsorbed even though dry gas is used after the initial preloading step.

A SETARAM Sensys Evo thermogravimetric analysis (TGA) instrument was used for several focused tests with the purpose of assessing sorbent performance and operational risk. The tests include the CO_2 working capacity in a simulated 4-BMS cycle, CO_2 capacity recovered after water exposure and reactivation at various temperatures, and water vapor adsorption. The available controls allowed for a study of the cyclic working capacity of CO_2 and/or water vapor in a N_2 purge between vacuum and 1 atm and at temperatures from 10°C to 350°C. The programmable controls of the system enables a sequence of pressures, temperatures, and concentrations that match the equilibrium segments of 4-BMS system operation. The risk assessment of candidate sorbents can be ascertained from introduction of water and observing the subsequent recovery of performance. The results can guide future 4-BMS designs and improve the operation of CDRA.

Thermal recovery profiles were obtained with the SETARAM instrument. Samples are initially saturated with moisture through exposure to ambient lab air as a representative worst-case scenario. Samples then undergo successively hotter activation cycles with adsorption of CO_2 at 25°C or 10°C immediately afterwards to probe extent of performance recovery. Additionally, a series of fifteen cycles at simulated-CDRA adsorption and desorption conditions and times was applied to a separate, water-laden sample and the final capacity is shown.

Simulated 4-BMS profiles were measured with the SETARAM instrument. A small-scale test that mimics the adsorption and desorption segments was designed and used to calculate a working capacity for each of a number of cycles. The purpose of this test is not to observe slow degradation mechanics such as dusting or trace contamination, but rather to determine whether the sorbent can operate well in a non-ideal operating environment. The first cycle of each of these tests was an activation at 350°C to observe the initial, maximum adsorption capacity and ensure comparative adsorption to reference isotherm values. After this, temperature profiles mimic what is found in a 4-BMS CO_2 sorbent bed. A dry scroll vacuum pump is used to evacuate the sample cell for the first half of the desorption segment of each cycle.

III. Results and Discussion

A. Sorbent structural properties

This work represents the summary of the ongoing sorbent screening and characterization efforts to determine the best candidate(s) for use in 4-BMS-X. Thus this work will focus mostly on the final data while referring to past works when possible. Testing with humidified samples is described in the work by Watson[10] regarding sorbent humidity conditioning.
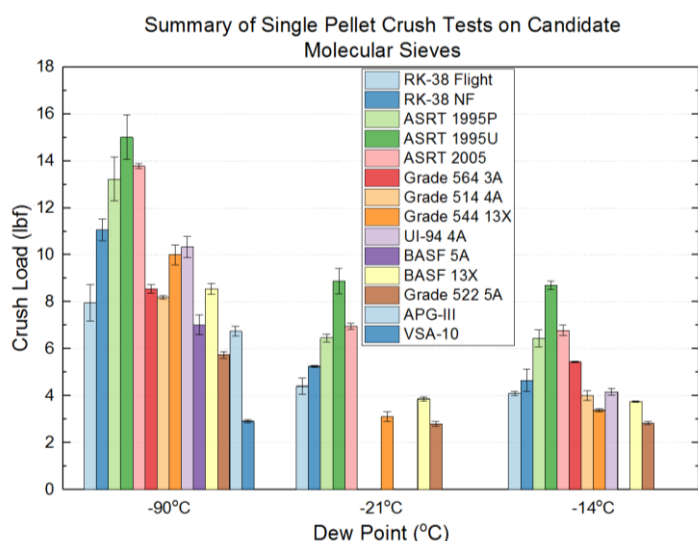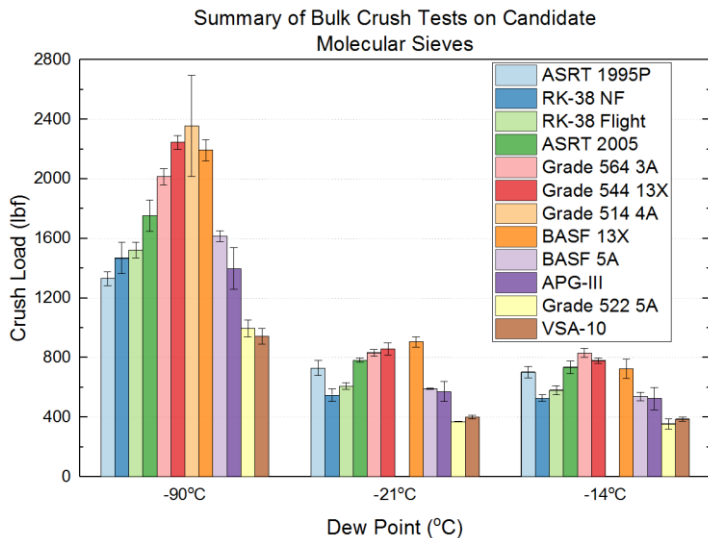

Figure 2. Summary of single pellet crush testing for desiccant and CO_2 sorbent materials which have flown in various CDRA systems and candidate sorbents for future 4-BMS systems. Several tests have not yet been measured due to time constraints.

Single Pellet Crush Test

Single pellet crush testing consists of three sets of fifty individual pellets from a sample crushed one at a time between two flat platens. The test apparatus and procedure is described in greater detail in the work by Watson.[5] The dry single pellet crush test results, statistical variances, the percentage of the pellets that dusted, and the mean force to cause dusting are used for the initial screening of candidate sorbents. The summary of pellet crush strengths grouped by moisture conditioning are shown in Figure 2.

The data presented here is a summary of the previous works by Watson[5] and Knox.[6] The strongest pellets which simultaneously show the most resistance to generating dust during a crush test are considered the prime candidates while those that generate significant dust with only mild crush loads are excluded. Due to the large time requirement for these tests, further tests were only conducted as necessary.

Figure 3. Summary of bulk crush testing for desiccant and CO_2 sorbent materials which have flown in various CDRA systems and candidate sorbents for future 4-BMS systems. Taller bars represent more favorable crush resistance. Humidity conditioned results for Grade 514 4A were not available at publication.

Bulk Crush Test

The bulk crush test differs from the pellet crush strength by simulating how a compressive load applied to a packed bed can damage the sorbent material. The test apparatus and procedure is described in greater detail in the work by Watson[5]. Often, the trends between material performance for bulk crush differs from single pellet crush testing. Bulk crush testing is considered to be more representative but requires much more material than is available with a small sample from a vendor. The summary of results are shown in Figure 3.

Attrition Test

The attrition test provides information on the production of dust by collisions between particles. It is possible for particles to be put in motion by mere eddy currents in a void of a packed bed in the microgravity environment found on orbit. Despite the fact that the packed bed in a 4-BMS system is compressed and a spring-loaded baffle plate is used to accommodate any settling, some voids may occur. Within these voids, particle collisions would constantly occur which could quickly generate dust and lead to system shutdown. Therefore, low attrition rates are a key factor to consider in sorbent selection. Figure 4 shows the results of the attrition testing.

Two materials are listed in this data set that have not been shown before. Grade 544 'C' 13X is simply a recently acquired batch. Grade 544-GR 13X is a subset of the extensively studied batch of Grade 544 13X where the GR suffix indicates a graphite coating according to patent[11] which provided data indicating a large reduction in pellet attrition. A large reduction was observed for humidity conditioned samples but an opposite and undesired effect was observed for dry material.
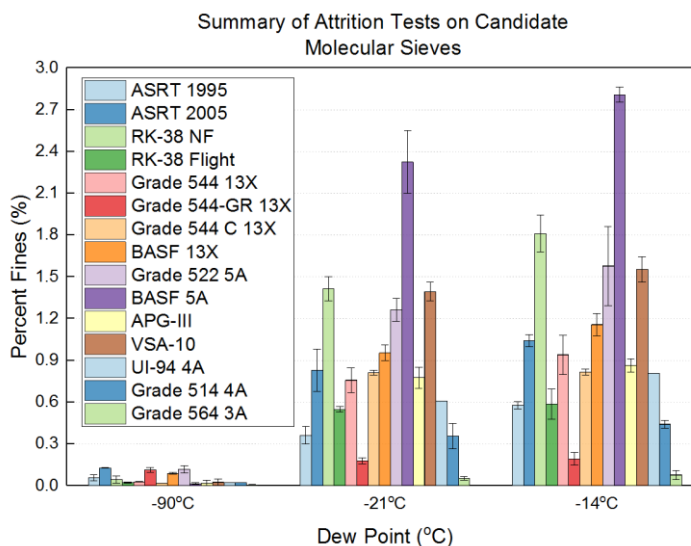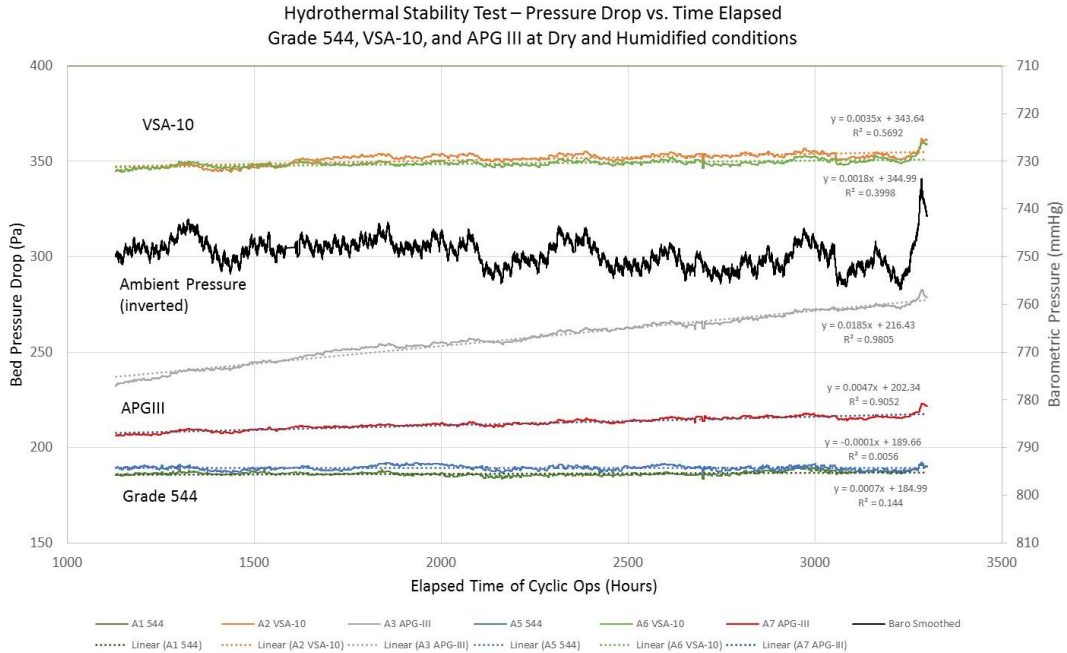
Hydrothermal Stability Test

The HST was designed with the purpose of measuring sorbent breakdown due to thermal cycling. The pressure drop increase that is measured for each sorbent over time can be reduced to a linear fit as shown in Figure 5. The initial pressure drop of the bed is an intrinsic function of the pellet size, shape, and uniformity. The slope, which is pressure drop vs time of these traces, is caused by changes in the bed that restrict air flow. One the theorized causes is the gradual development of cracks due to cycles of heating and cooling with differing coefficients of thermal expansions between zeolite crystals and binder within the pellet which leads to dusting and flaking. Another theorized cause is crushing due to the thermal expansion and contraction of the entire bed of pellets. Although no sole cause has been identified, the result is production of dust which clogs

Figure 4. Summary of attrition testing for desiccant and CO_2 sorbent materials which have flown in various CDRA systems and candidate sorbents for future 4-BMS systems. Shorter bars represent more favorable properties. Additional tests to determine error bars for UI-94 were not available at publication.

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Hydrothermal Stability Test – Pressure Drop vs. Time Elapsed
Grade 544, VSA-10, and APG III at Dry and Humidified conditions

Figure 5. Example chart of raw data from the HST test stand operation on three pairs of materials. Due to the inverse effect of backpressure from ambient conditions in the facility, the barometric pressure is plotted on a reverse scale for reference as it appears to correlate well with test data excursions. The large pressure excursion at the end corresponds to a notable weather pattern.

filters and flow paths leading to higher pressure drop through the bed. Figure 6 shows the combined results of several HST tests on the materials which have been under consideration up to now. Of particular note is that the previously used sorbents show some of the worst pressure drop rise which indicates most new candidate sorbents will likely perform well in long-term, cyclic operation.

Numerous candidate sorbents show significantly less pressure drop issues than the previously used ASRT and RK-38 sorbents. ASRT was considered a viable sorbent for long-duration (up to 3 year) missions while RK-38 led to system shutdown within 6 months. Notable candidates are Grade 544 13X, BASF 13X, and VSA-10 LiLSX which each showed very little pressure drop rise over the length of the experiments. For VSA-10, this is a surprising contrast to the pellet crush testing where it was exceptionally weak. Considered as a whole, these test results show that no single structural test is predictive of packed bed reliability.

The negative value for the Poly-IEX sample in dry N_2 was attributed to the proprietary and experimental preparation method of the bed which was an immobilized, polymer-bound sorbent. The slight pressure drop for Grade 544 13X in dry N_2 can be attributed to the effect of ambient pressure changes across several months thus it is equivalent to zero.

Among the four clay-bound zeolite pellets used as flight materials so far, the HST correlates quite well with in-flight system behavior. These materials are ASRT 1995, ASRT 2005, RK-38, and Grade 544. The HST tests conducted on
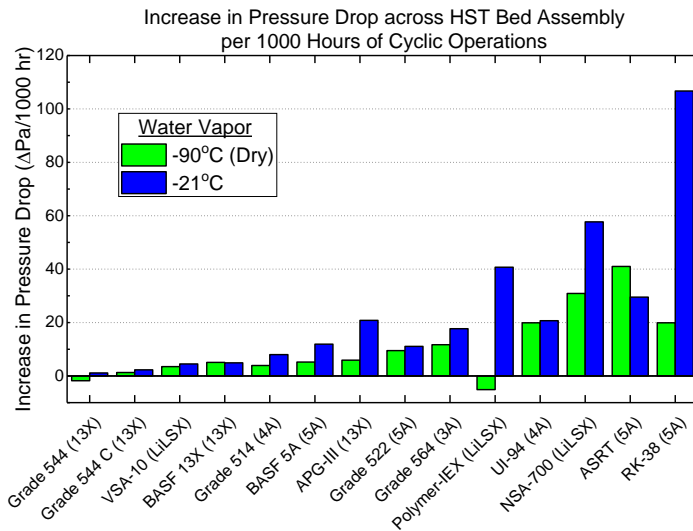
Figure 6. Summary of pressure drop vs time for all materials measured in the HST to date. Shorter bars in both dry and humidified conditions is favorable for long-term stability under thermally cyclic operation.

these materials agrees with the observations from flight CDRA teardowns: RK-38 produced significant dust, both ASRT versions produced some dust but not enough to cause a shutdown due to screen blinding, and Grade 544 has never been reported to show problems.

<u>Sorbent Structural Property Summary</u>

The five candidate sorbents considered between the 2016 and 2017 downselects were: Grade 522 5A, Grade 544 13X, BASF 13X, APGIII 13X, and VSA-10 LiLSX. The 2016 downselect eliminated many candidates due to poor performance in one or more structural tests and the increased risk that may go with it. Among these remaining five, Grade 522 5A was retained as a marginal candidate due to the similar zeolite to presently used sorbents in CDRA. APGIII and VSA-10 will be shown later to possess exceptional adsorption capacity but at the cost of pellet integrity. Grade 544 13X and BASF 13X show very similar performance and the least overall risk due to the various theorized causes of pellet dusting. The 2017 downselect produced Grade 544 as the selection due to its favorable history in use on orbit.

B. Desiccant selection

The collaborative efforts between experimentation and modelling for design of a 4-BMS system have produced some interesting revelations allowing for significant performance increases. One of these is the reduction of residual desiccant used in the beds due to the additional effect of parasitic CO_2 capture. In essence, CO_2 is held-up in the desiccant bed and then returned to the cabin instead of separated to space or to other closed-loop systems. System-wide CO_2 removal efficiency can be increased significantly if the residual desiccant did not adsorb much CO_2 during a cycle. Therefore, the residual desiccants under consideration are the presently used 13X zeolite, 3A and 4A zeolites, and a mesoporous alumina. The 4A and 13X zeolites adsorb CO_2 in the dry zones of the desiccant bed but the adsorption rate and capacity is less for 4A. The 3A zeolite adsorbs virtually no CO_2 due to pore size restrictions and the alumina shows only minimal CO_2 adsorption compared to the zeolites.

<u>Water Vapor Isotherms</u>

In collaboration with Ames Research Center,[12] the measurement and fitting of water vapor isotherms on the bulk and residual desiccants have been underway. Partial results of this effort are shown in Figure 7. The data is used as inputs for simulations of the residual desiccant layer in a 4-BMS system while other properties are validated against the breakthrough test results. These simulation efforts are described in detail in the work by Coker[9] and the continuing efforts are described by a companion paper yet to be published by Giesy.[13] Particular focus has been on zeolites due to the extreme affinity for adsorbing water vapor and difficulty of measuring the gas phase concentration of water at these levels.
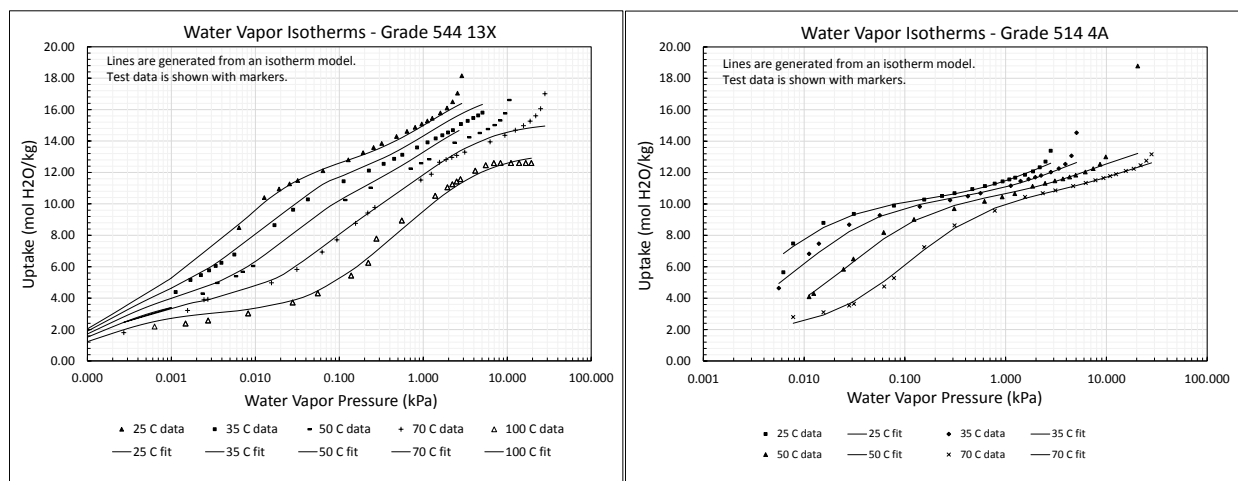

Figure 7. Water vapor isotherms measured on a DVS Vacuum instrument at ARC on Grade 544 13X and Grade 514 4A. The discrepancies shown throughout the data set can be attributed to the extreme difficulty in precise measurement of the zeolite-water vapor system. Even at low water vapor partial pressures, significant water uptake is observed leading to long test times and increased chance of compounding errors.

Design of the desiccant beds with regard to water can be reduced to two major design points: length of time for effective drying and effectiveness over many cycles. The latter is intrinsically tied to the operation of the system and studies are just beginning. The former design point can be approximated by simple tests allowing for a ranking of candidate sorbents. In the previous work[6], candidate residual desiccants were subjected to a step-change introduction of a low dewpoint N_2 stream (roughly -40°C). The results showed that 13X zeolite remained by a large order the best option for capturing water below detectable limits for the longest time. The next best candidate was 4A zeolite at only half the effectiveness of 13X. It also showed that 3A zeolite suffered from rate limitations where an almost immediate breakthrough of traces of water were observed despite having a similar final capacity to 4A zeolite.

In order to better compare the residual desiccant candidates, a test with silica gel and zeolite layers was conducted which approximates the structure of the current desiccant beds. The layered test beds are subjected to a step-change introduction of the highest achievable dewpoint N_2 stream in this test stand (roughly -2°C). The silica gel layer removes most of the water resulting in a steadily increasing water vapor content to the residual desiccant layer. In order to deconvolute the effect of the layers, two beds were tested in parallel on a pair of parallel ports on the HCS. Both beds contained the same amount of silica gel while one had an additional layer of residual desiccant. Figure 8 shows the plots obtained directly from the data record.

The results of the layered desiccant test reinforced the ranking derived from the standalone residual desiccant tests. The best residual desiccant remains the 13X zeolite while 4A zeolite showed slight improvement and may be viable as a substitute. Based on this and previously reported[6] testing, the 3A zeolite and alumina are not viable for maintaining an extremely dry gas stream for a significant amount of time. The design choice between 4A and 13X zeolites remains to be determined and will require a significantly more capable instrument to approximate a 4-BMS
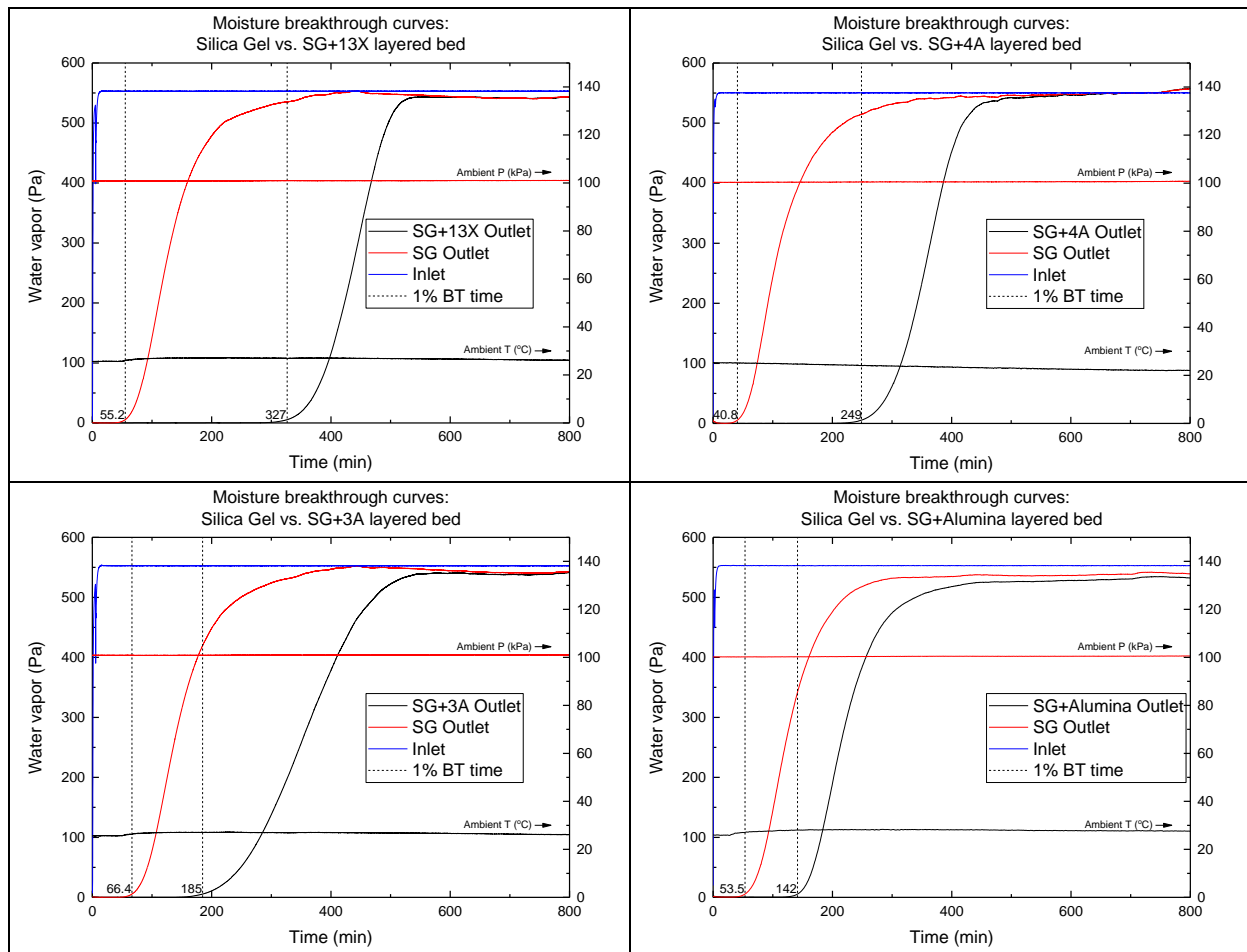
Figure 8. Qualitative comparison between a series of desiccant candidates in a layered bed configuration with silica gel (SG). The best candidate desiccants to fully dry the incoming cabin air for a 4-BMS system will maintain a dew point below detectable limits for the longest period of time. The four materials tested are Grade 544 13X, Grade 514 4A, Grade 564 3A, and F200 Alumina.

system or an extremely refined model with well-resolved inputs. Since the inlet absolute humidity was roughly 550 Pa, which is less than half of the expected 4-BMS-X operating point of 1.2 kPa, these conclusions will be confirmed through testing in another instrument with higher humidity capabilities.

Water Vapor Breakthrough Testing with Centerline Sampling

The diameter of the CBT test article is 1.375" in diameter which is roughly 14 pellets across. This scale means that the effects of gas flow near the walls will be significant. Near the wall, which is defined as roughly 2 pellet diameters, the packing density is reduced and thus gas flow is less impeded and moves more rapidly without interacting with sorbent material. The measurements conducted with this test stand in the past relied on a concentration sampling of the gas far downstream of the end of the bed. At this point, the gas that

Figure 9. Water vapor breakthrough on Grade 544 13X measured with the CBT test stand. The resulting temperature profile and concentration profiles of total mixed flow and the sampled centerline flow are shown.

flows through the center of the bed and the gas that flows along the walls are thoroughly mixed. Deconvoluting these two flow regimes is important to accurately model the performance of the sorbent and further to predict the behavior of a much narrower or larger system.[14] In the case of the CO_2 sorbent beds in CDRA with very narrow heater core channels, the wall effects are very large whereas the desiccant bed sees only insignificant contributions.

The water vapor breakthrough curves such as the representative one shown in Figure 9 are used to refine the simulation model. A centerline sampling port was added to the test article to measure the gas concentration without the effects of wall channeling observed in measurement of the mixed, bulk flow downstream of the bed. The two breakthrough curves from a single test are shown together where the centerline curve is more representative of the behavior of a bed as large as one in the 4-BMS. Notably, the centerline and mixed breakthrough plots intersect near the completion of breakthrough which is attributed to thermal effects in the center of the bed versus near the aluminum bed walls. A large temperature increase due to the high capacity and high heat of adsorption of water onto zeolite supports this assumption. This behavior will be important for simulation validation as it shows the complexity of zeolite/water adsorption.
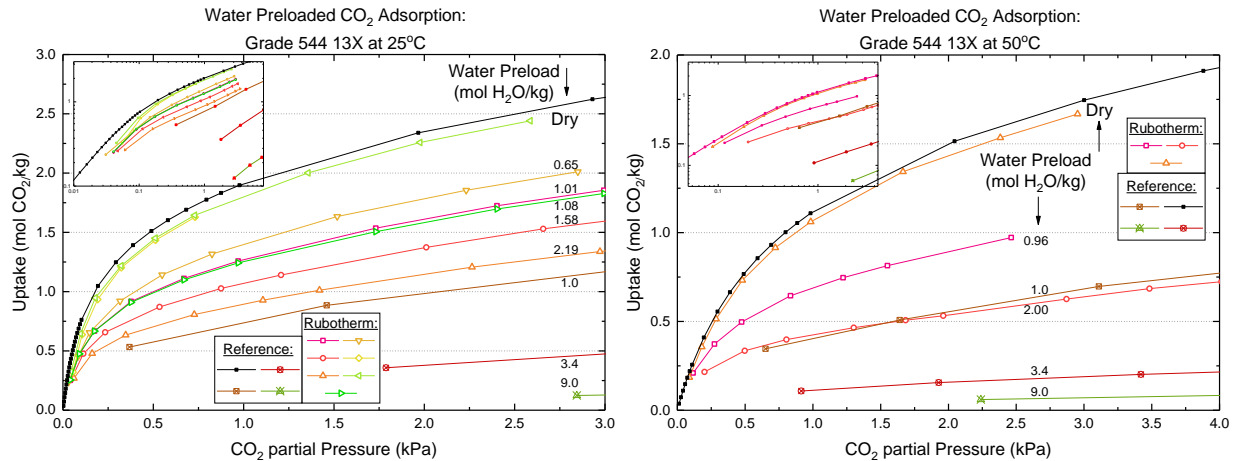
Water Preloaded CO_2 Isotherms

Recently, control and measurement of water loading and CO_2 adsorption has become available. Two temperatures have been tested so far as well as comparisons to previously published data. The preliminary results are shown in Figure 10.

The first comparison to be made is between the dry isotherms obtained in the instrument and reference data. The measured uptake difference is roughly 5% below the reference value which was found at both the start and end of the test series. The second comparison is to published water preloaded CO_2 adsorption tests where an incomplete desorption due to low achievable temperature may have led to a higher preloading of water than calculated. The results obtained here show that the reference preloading of 1.0 mol H_2O/kg is closer to the new measured preloading of 2.19 mol H_2O/kg. Therefore, the difference between the newly measured isotherms and this reference is approximately 1.5 mol H_2O/kg preloading, i.e. a preloading of 1.0 is in fact 2.5.

Further analysis of these tests show some imperfections, notably the first one or two data points for the dry isotherms. This error is attributed to a large adsorption step which leads to incomplete equilibration and the low remaining gas phase concentration of CO_2 which approaches measurement limitations. Subsequent points are not affected by this error as the adsorption steps are smaller thus equilibrium is more quickly achieved and concentration measurement is relatively easy.
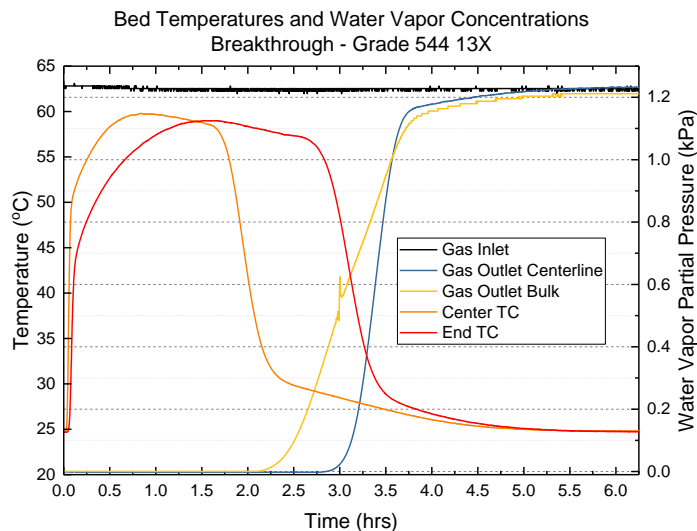
Figure 10. Water preloaded CO_2 isotherms on Grade 544 13X at 25°C and 50°C are shown with open symbols. Inset shows the same data on a log-log plot. Reference isotherms for dry CO_2 adsorption[12] are solid black squares and open symbols with a cross are reference water preloaded isotherms.[15]
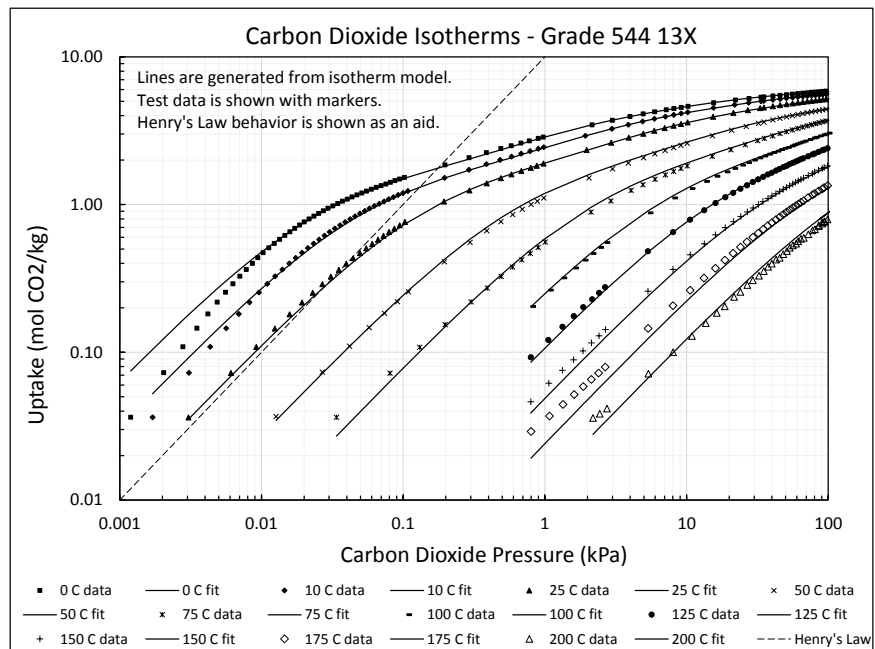
Continuing these tests at higher temperatures is necessary to accurately model the desiccant bed behavior where water and CO_2 interact with the zeolite sorbent. The desorption of this material is conducted with a hot purge, therefore temperatures up to 200°C will need to be tested, but at this time only 25°C and 50°C have been completed. The results for adsorption at 50°C and comparison to reference isotherms are also shown in Figure 10. The observable behaviors are similar to what was previously discussed but with the reference isotherm for 1.0 mol H_2O/kg preloading being overlapped by the new 2.00 mol H_2O/kg preloaded CO_2 isotherm.

C. CO₂ Sorbent selection

CO₂ Isotherms

A collaborative effort between MSFC and ARC for measurement and fitting of high-fidelity CO_2 isotherms has been underway. Despite measurement with different systems from different manufacturers, strong agreement has been found when test procedures are crafted to specifically handle these sensitive materials. Exclusion of water is paramount and thus necessitates an activation procedure that is different from the manufacturer's standard. Also, careful control of sample inventory across the centers is needed as batch-to-batch variations have been observed to be large.

All tested CO_2 sorbents have been measured across the entire range of operating temperatures

Figure 11. Carbon Dioxide isotherms measured in a collaborative effort between MSFC and ARC overlaid with the results of a 3-site Langmuir model fit to the data set. Isotherms up to 75°C were measured at ARC while isotherms from 100-200°C were measured at MSFC.

encountered in 4-BMS operation and fit with a temperature-dependent 3-site Langmuir model. This model was chosen due to the ability to very precisely match the data, ease of differentiation for modelling, and reduction to Henry's Law at low pressures. The downside of this model is that it has upwards of 12 fitting parameters which means a large data
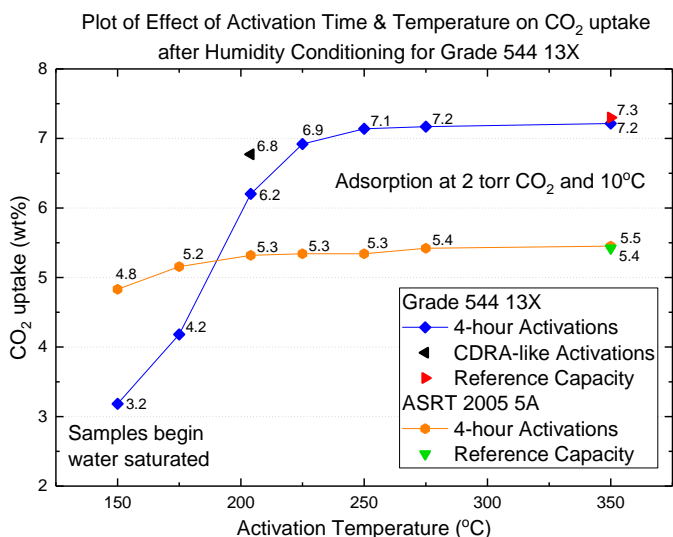
set is required to eliminate degrees of freedom in the fit and not arbitrarily overfit the data. By definition, overfit data can show very poor predictive behavior as some of the parameters are arbitrary.

The bulk of the measurements between 0 and 75°C were conducted on the ARC instrument. These tests compared favorably with older data obtained at MSFC. The ARC data was selected as the achievable pressures were generally lower and more clearly showed Henry's Law behavior in the measurements. The MSFC data was retained for isotherms from 100°C to 200°C. The results of these efforts are shown in Figure 11.
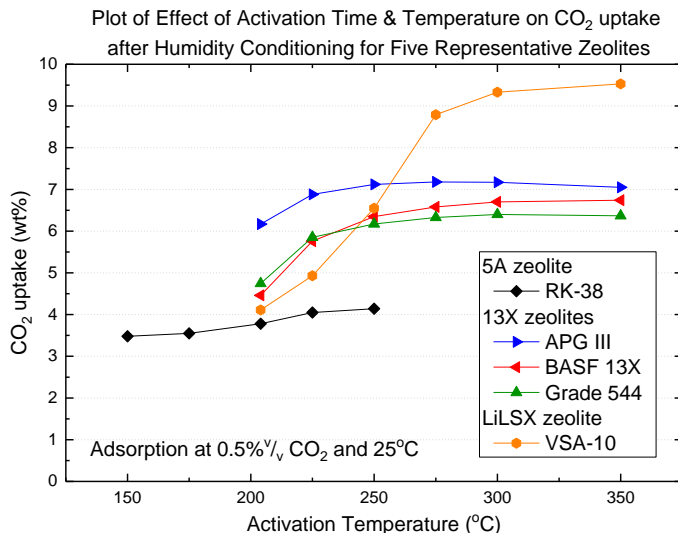
Thermal Regeneration and Recovery Profiles

A design objective of the next generation 4-BMS is a reduced activation temperature in the CO_2 sorbent bed, but this comes with the risk of incomplete regeneration or a build-up of trace water in the bed over time. A simple test was

Figure 12. Results of sequential activation testing on various candidate sorbents. The three types of zeolites show a minimum recovery temperature to achieve 95% of complete capacity which may correlate to the chemistry of the zeolite. Notably, at 225°C, nearly complete recovery of CO_2 working capacity for each of the 13X zeolites is observed.

designed to assess this risk by testing a water loaded sample and sequentially activating at increasing temperatures for 4 hours then cooling and adsorbing CO_2. This activation time was selected as an attempt to represent an extended bakeout of a bed to recover from a major water leak or other malfunction. The adsorption temperature was selected to be 25°C due to system limitations at that time. A partial set of this work was published in the predecessor to this work.[6] Starting from currently achievable temperatures of 204°C, a profile was developed to determine what temperature is required to achieve roughly 95% of the full adsorption capacity and is shown in Figure 12.

All the X-type zeolite sorbents under consideration showed higher capacity than RK-38 5A zeolite after 204°C activation, which indicates any of them would be a favorable replacement. Surprisingly, VSA-10 shows only a marginal improvement over 5A at 204°C and requires upwards of 275°C to recover the exceptionally high capacity observed with isotherms. The three 13X zeolites show significant recovery of CO_2 capacity at 204°C and only require

a little more thermal intensity to achieve full capacity in the 4 hour window. As a result of the recent downselect, sorbent characterization has come to focus on Grade 544 13X and additional review of this material was conducted. In addition to recreating the 4-hour bakeout test with newer system capabilities, a test of the performance after regeneration profiles which simulate CDRA was conducted. These two tests are shown for Grade 544 13X and ASRT 2005 5A along with the reference values from isotherms in Figure 13.
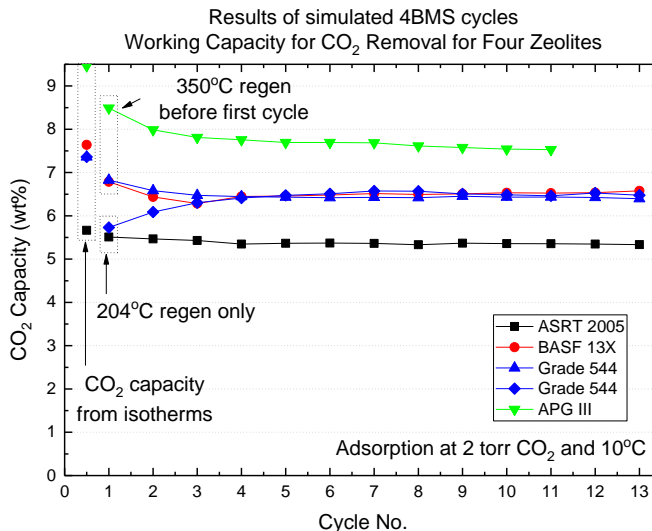
After several cycles in the relatively mild temperatures of a CDRA-like operating cycle, the working capacity reached a cyclic steady state very close to maximum performance. Thus higher temperatures simply accelerate the removal of water and recovery of CO_2 capacity.

Figure 13. Results of sequential activation testing on Grade 544 13X and ASRT 2005.

These tests provide assurance that Grade 544 13X will restore to nearly full capacity through normal operating cycles, thus it appears to be fault tolerant. This test describes the general behavior of candidate sorbents in a known fault situation and allows comparison to various system design temperature limitations.
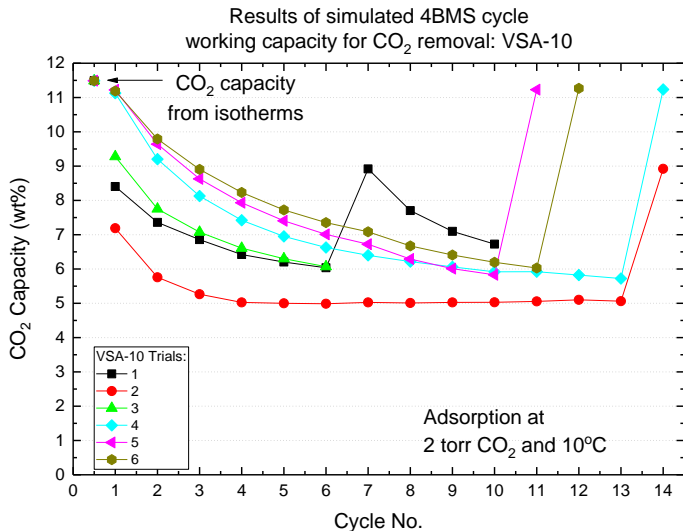
Simulated 4-BMS Operation

Single component adsorption measurements provide the first and most precise data for determining the properties of sorbents to be used. Further study is required to determine how these materials behave in cyclic operation. Simulating the temperature and pressure swings of a 4-BMS CO_2 sorbent bed is critical to measuring a realistic working capacity. The profiles of these tests are shown in Figure 14.

All four materials shown in Figure 14 appear to reach a cyclic steady state after 3 or 4 cycles but at a reduced performance

Figure 14. Plot of working capacity for candidate materials in cyclic operation which simulates the adsorption and desorption in a 4-BMS system. Several cases explored an ideal starting condition of complete activation at 350°C while two other cases showed the behavior when only 204°C is achieved.

level when compared to reference isotherm values. The three 13X zeolites show a reduced performance from the value obtained in dry isotherm tests or after a 350°C activation cycle. APGIII shows a higher cycling working capacity throughout the test series, indicating it would be a highly favorable candidate to reduce the size of 4-BMS CO_2 sorbent

Figure 15. Plot of working capacity for the strongest adsorbent tested, VSA-10, in cyclic operation which simulates the adsorption and desorption times and temperatures of a 4-BMS system. All cases began with the ideal starting condition of complete activation at 350°C. All test cases show a rapid loss of performance cycle-to-cycle and only appear to reach a cyclic steady state at roughly 35% of initial capacity. Various system and procedure modifications improved the initial performance but performance continuously decreased over the span of a few days for all tests until a high temperature activation was again used.

beds. Grade 544 13X and BASF 13X are nearly indistinguishable and ASRT shows a very level working capacity near the isotherm value. A very interesting result observed here as shown by the blue diamonds is the recovery of performance for a 13X sorbent without the need for a temperature higher than 204°C even after humid air exposure.

Several limitations to these tests should be noted, especially the possibility of water diffusion into the measurement cell during each cycle. The small sample size of less than a dozen pellets (~60mg) means that any small source of contamination that goes unnoticed in tests of ~100g would have a disproportionately large effect here. This was observed most remarkably in the cycle-to-cycle profiles of every VSA-10 test shown in Figure 15 Possible causes included diffusion through flexible rubber tubing and rubber O-rings when the vacuum pump had reached ultimate vacuum or simply the traces of water present in bottled N_2 that are well within specification. For reference, the dew point at the outlet of a 4-BMS desiccant bed is drier than the specification of bottled UHP N_2. Additionally, the low concentration of
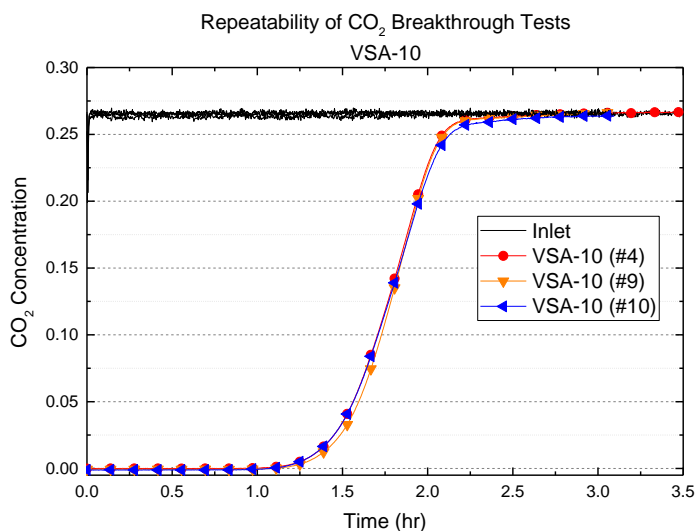
CO2 in the supplied gas necessitates a small sample size or else the sample would not equilibrate in the short cycle time of a 4-BMS system.
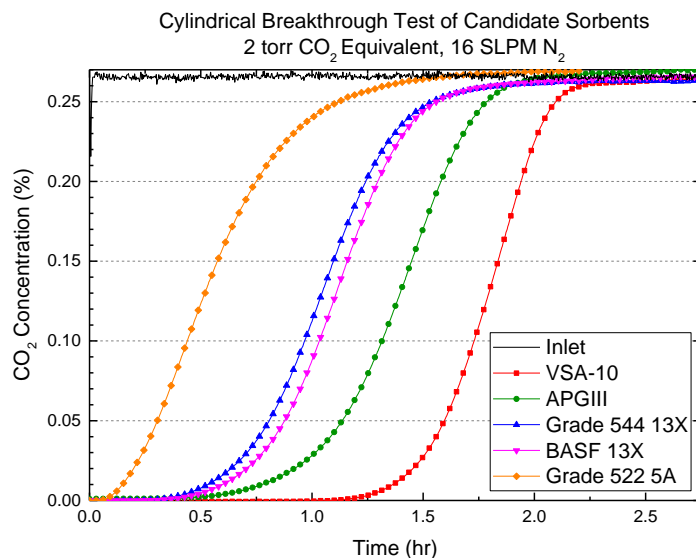
From these results, VSA-10 could not be considered a candidate if the system is limited to 204°C. Due to numerous material incompatibilities, ranging from insulation to rubber O-rings to aluminum, higher temperatures would require extensive redesign of the 4-BMS-X system. The other 13X zeolite sorbents also showed a slight decrease from the initial activation cycle but this levels out to a cyclic steady-state performance that exceeded the previously used 5A sorbent, ASRT. This behavior provides a high level of confidence that system volumes can be reduced and/or improve throughput without severe risk.

<u>CO2 Breakthrough Testing with Centerline Sampling</u>

Selection and characterization of the CO2 sorbents in a packed bed configuration is necessary for design of any separation system. Between the 2016 and 2017 downselects, five zeolites were still under consideration: one 5A, three 13X, and one LiLSX. The direct comparison of bulk breakthrough curves of these five materials is shown in Figure 16. VSA-10, the LiLSX material, performs far better than the rest, but it was shown above to be quite sensitive to water and difficult to regenerate. In this large packed bed configuration, trace water will only affect an insignificant portion of the bed over the hours and days of testing. The repeatability of these tests to support this claim is shown in Figure 17 where the highly sensitive VSA-10 material showed identical breakthrough curves.


Figure 16. Breakthrough curves for the five candidate sorbents identified in the downselect of early 2016. Inlet conditions are 2 torr equivalent, CDRA nominal inlet velocity equivalent, and 25°C in dry N_2.

Figure 17. Breakthrough curves for most sensitive sorbent material, VSA-10, showing the high level of repeatability between different test preparations and between repeated tests of a single bed. These results show the high level of consistency of the CBT test stand. Inlet conditions are 2 torr equivalent, CDRA nominal inlet velocity equivalent, and 25°C in dry N_2.

Each of these tests included a centerline breakthrough measurement with the results for Grade 544 13X shown in Figure 18. This figure shows two sets of breakthrough plots measured with two different test preparations and with two different instruments to measure the concentration of CO_2 in the centerline flow stream, first a GC and later an infrared transducer. The close similarity of these two data sets provides reassurance for the methods employed.

The differences between centerline and mixed flow appear to be less pronounced here than shown in Figure 9 which this is due to a larger adsorption rate and capacity for. Since adsorption models are derived on assumptions that most closely match the center of a packed bed, this set of results will enable refinement of the CO_2 sorbent bed behaviors and simulation of larger scale systems.
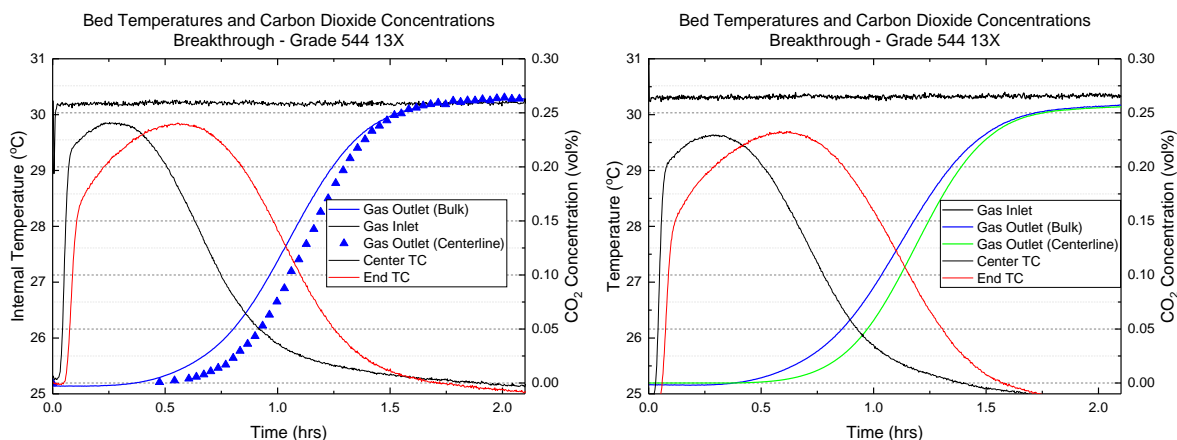
Figure 18. The bulk and centerline breakthrough curves and temperature profile for 2 torr CO_2 flow in dry N_2 at 25°C and 0.2 m/s superficial velocity for Grade 544 13X. The centerline breakthrough curve plotted on the left was obtained with a GC sampling once every 2 minutes. The centerline breakthrough curve plotted on the left was obtained with an optical sensor measuring continuously.

IV. Conclusions and Future Work

For the guard layer and among the bulk desiccants, the results indicate that no changes need to be made for CDRA and for future 4-BMS systems as the combination of properties found with the current materials is equal to or better than the tested alternatives. Among the residual desiccants, the present 13X zeolite remains the primary option, although further study of cyclic water vapor and carbon dioxide adsorption may indicate the value of a different residual desiccant such as a 4A zeolite. Structural characterization indicates that several options, including 3A and 4A zeolite, would be mechanically reliable.

The set of CO_2 sorbents was pared down to five during the 2016 downselect: one 5A, three 13X, and one LiLSX zeolite. Recent direction indicated that the overarching requirement is to minimize dusting and eliminating, to the extent possible, dust-related equipment failures and shutdowns. Two 13X zeolites among the previous five could qualify for this requirement, Grade 544 13X and BASF 13X. These two materials showed roughly equivalent structural and adsorption properties, but Grade 544 has been used for many years in the desiccant beds onboard the ISS without evidence of dusting. Thus the evidence of reliable past performance coupled with the indications from all ground testing showing satisfactory performance and no apparent propensity to generate dust means this material is the primary CO_2 sorbent selection.

For a new 4-BMS system, smaller CO_2 sorbent beds can be designed with the selection of this 13X-based sorbent due to improved capacity and faster adsorption kinetics over the previously used 5A materials. The simulated cyclic operation with a regeneration temperature of 204°C indicates that 13X zeolites can recover 90-95% of full CO_2 removal capacity from a worst-case water exposure event. The results obtained in this work help to guide this risk assessment and thus future 4-BMS designs.

Future work includes completion of the current data sets of structural properties and verifying the multi-temperature CO_2 and H_2O adsorption isotherms. Additional focus is required on the selection of residual desiccants which show less parasitic CO_2 adsorption outside of the CO_2 separation bed while fully desiccating the inlet air. Study of these materials will require cyclic testing in a layered configuration as well as development of co-adsorption isotherms. Ground testing has indicated that Grade 544 13X will have sufficient performance, be fault tolerant, and mechanically robust while also very likely to remain commercially available thus minimizing all of the previously known risks from the previous CDRA sorbents.

V. Acknowledgements

References

[1]"NASA's Journey to Mars: Pioneering Next Steps in Space Exploration." 2015.

[2]Allen, J. G., MacNaughton, P., Satish, U., Santanam, S., Vallarino, J., and Spengler, J. D. "Associations of Cognitive Function Scores with Carbon Dioxide, Ventilation, and Volatile Organic Compound Exposures in Office Workers: A Controlled Exposure Study of Green and Conventional Office Environments," *Environ Health Perspect*, 2015.

[3]James, J. T., Meyers, V. E., Sipes, W., Scully, R. R., and Matty, C. M. "Crew health and performance improvements with reduced carbon dioxide levels and the resource impact to accomplish those reductions," *41st International Conference on Environmental Systems*. Portland, Oregon, 2011.

[4]Satish, U., Mendell, M. J., Shekhar, K., Hotchi, T., Sullivan, D., Streufert, S., and Fisk, W. J. "Is CO2 an indoor pollutant? Direct effects of low-to-moderate CO2 concentrations on human decision-making performance," *Environ Health Perspect* Vol. 120, No. 12, 2012, pp. 1671-7.

[5]Watson, D., Knox, J. C., West, P., and Bush, R. "Sorbent Structural Testing of Carbon Dioxide Removal Sorbents for Advanced Exploration Systems," *46th International Conference on Environmental Systems*. Vienna, 2016.

[6]Knox, J. C., Cmarik, G., Watson, D., Wingard, C. D., West, P., and Miller, L. A. "Investigation of Desiccants and CO2 Sorbents for Advanced Exploration Systems 2015-2016," *46th International Conference on Environmental Systems*. Vienna, 2016.

[7]Knox, J. C., Gostowski, R., Watson, D., Hogan, J. A., King, E., and Thomas, J. "Development of Carbon Dioxide Removal Systems for Advanced Exploration Systems," *International Conference on Environmental Systems*. AIAA, San Diego, 2012.

[8]Knox, J. C., Gauto, H., and Miller, L. A. "Development of a Test for Evaluation of the Hydrothermal Stability of Sorbents used in Closed-Loop CO2 Removal Systems," *International Conference on Environmental Systems*. Bellevue, Washington, 2015.

[9]Coker, R. F., and Knox, J. C. "Predictive Modeling of the CDRA 4BMS," *46th International Conference on Environmental Systems*. Vienna, 2016.

[10]Watson, D., Knox, J. C., West, P., Stanley, C., and Bush, R. "Sorbent Structural Impacts due to Humidity on Carbon Dioxide Removal Sorbents for Advanced Exploration Systems," *45th International Conference on Environmental Systems*. Bellevue, Washington, 2015.

[11]Acharya, A., and BeVier, W. E. "Attrition resistant molecular sieve." U.S. Patent 4,526,877. filed Sep 28, 1984.

[12]Huang, R., Belancik, G., Jan, D., Cmarik, G., Ebner, A. D., Ritter, J., and Knox, J. C. "CO2 Capacity Sorbent Analysis using Volumetric Measurement Approach," *47th International Conference on Environmental Systems*. Charleston, 2017.

[13]Giesy, T. J., Coker, R. F., and Knox, J. C. "Virutal Design of a 4-Bed Molecular Sieve for Exploration," *47th International Conference on Environmental Systems*, 2017.

[14]Knox, J. C., Ebner, A. D., LeVan, M. D., Coker, R. F., and Ritter, J. A. "Limitations of Breakthrough Curve Analysis in Fixed-Bed Adsorption," *Industrial & Engineering Chemistry Research*, 2016.

[15]Wang, Y., and LeVan, M. D. "Adsorption Equilibrium of Binary Mixtures of Carbon Dioxide and Water Vapor on Zeolites 5A and 13X," *Journal of Chemical & Engineering Data* Vol. 55, No. 9, 2010, pp. 3189-3195.