Development of Carbon Dioxide Removal Systems for Advanced Exploration Systems

James C. Knox, Diep Trinh, Rudy Gostowski, Eric King, Emily M. Mattox, David Watson, John Thomas
NASA Marshall Space Flight Center, Huntsville, Alabama, 35812, USA

***"NASA's Advanced Exploration Systems (AES) program is pioneering new approaches for rapidly developing prototype systems, demonstrating key capabilities, and validating operational concepts for future human missions beyond Earth orbit" (*NASA 2012*).* **These forays beyond the confines of earth's gravity will place unprecedented demands on launch systems. They must not only blast out of earth's gravity well as during the Apollo moon missions, but also launch the supplies needed to sustain a crew over longer periods for exploration missions beyond earth's moon. Thus all spacecraft systems, including those for the separation of metabolic carbon dioxide and water from a crewed vehicle, must be minimized with respect to mass, power, and volume. Emphasis is also placed on system robustness both to minimize replacement parts and ensure crew safety when a quick return to earth is not possible. Current efforts are focused on improving the current state-of-the-art systems utilizing fixed beds of sorbent pellets by seeking more robust pelletized sorbents, evaluating structured sorbents, and examining alternate bed configurations to improve system efficiency and reliability. These development efforts combine testing of sub-scale systems and multi-physics computer simulations to evaluate candidate approaches, select the best performing options, and optimize the configuration of the selected approach, which is then implemented in a full-scale integrated atmosphere revitalization test. This paper describes the carbon dioxide (CO_2) removal hardware design and sorbent screening and characterization effort in support of the Atmosphere Resource Recovery and Environmental Monitoring (ARREM) project within the AES program. A companion paper discusses development of atmosphere revitalization models and simulations for this project.**

I. Introduction

Successful and efficient development of sorption-based separation technologies for future life support applications requires analytical, experimental, and modeling and simulation capabilities in numerous areas. Activities in the carbon dioxide (CO2) removal hardware design and sorbent screening effort being conducted as part of the ARREM project are presented in the following sections following a description of the generalized approach. Activities with a focus on computer modeling and simulation are discussed in a companion paper (Knox, Coker, Kittredge, Cummings and Gomez 2012).

II. Process Design Approach

In general, development efforts combine sub-scale testing, multi-physics computer simulations, full-scale testing stand-alone testing, and full-scale testing in an integrated atmosphere revitalization test. The overall ARREM project is described in another paper (Perry, Abney, Knox, Parrish and Roman 2012). The general process steps are shown below. However, since candidate technologies are at various technology readiness levels (TRL), this generalized process can only be applied where appropriate. For example, the initial integrated atmosphere revitalization (AR) testing will include a full-scale functionally-flight like replicas of the International Space Station CO_2 removal system.

1. Characterize candidate sorbents and compare directly with state-of-the-art sorbents. Select promising sorbent candidates for life support process of interest.
2. Develop new or modify existing mathematical models and computer simulations for process of interest.
3. Via simulation, optimize cyclic test configuration (e.g., canister design and cycle parameters).
4. Fabricate test article and execute test series. Evaluate sorbent efficacy for go/no go to next larger scale. Validate and refine simulation.

5. For promising sorbents, repeat steps 3 and 4 while increasing scale until full-scale for the process of interest is attained.
6. Incorporate the full-scale system into the integrated AR configuration and evaluate via integrated testing.
7. Provide technology solution to spacecraft flight system developer.

III. Sorbent Characterization and Screening

Sorbents by definition attract and retain sorbates. Understanding the mechanisms of sorption is necessary to apply the appropriate techniques for measurement of sorptive capacity, sorption kinetics, and selectivity. These measurements provide a means for initial sorbent screening and selection as well as critical input data for the development of computer simulations

Three sorbent types are of particular interest for the ARREM project: zeolites or molecular sieves, silica gels, and solid amines (or amines immobilized on a porous substrate). Table 1 provides the performance factors that are of interest for sorbent screening; also shown are those factors that provide inputs for computer simulations.

Table 1. Sorbent Performance Factors

Powder/Chemical Performance Factors	Screening Criteria	Simulation Input	Pellet/Structured Sorbent Performance Factors	Screening Criteria	Simulation Input
Micropore Diffusion	√	√	Macropore Diffusion	√	√
Pore Size Distribution	√		Pressure Drop	√	√
Surface Area	√		Pellet Crush Strength	√	
Single Gas Equilibrium Capacity	√	√	Bulk Crush Strength	√	
Mixed Gas Equilibrium Capacity	√	√	Spalling (Coated Metals)	√	
Heat of Adsorption	√	√	Friability	√	
Adsorption Kinetics (TGA)	√	√	Thermal Stability	√	
			Density	√	√

The first column of performance factors may be measured using sorbent powders or precursor amine liquid independent of the final sorbent format (that is, pellets, extruded monoliths, wash-coated structures, or immobilized amines). These performance factors should also be measured using the final sorbent format; by comparison with the powder or liquid data any performance reduction due to the pelletizing or coating process is readily identified. The second column of performance factors applies only to the final sorbent format. For the pelletized format, the structural stability factors (items 3 through 7 in the second group) is of special interest due to well-known issues with pellet dusting both in the chemical industry and in recent spacecraft life support experience (El Sherif and Knox 2005)

Sorbents of interest to the ARREM program are primarily zeolites or molecular sieves, silica gels, and immobilized amines. Figure 1 illustrates, from right to left, type A zeolite framework structure; zeolite crystals, and zeolite pellets. Figure 2 shows two forms of silica gels under consideration; a granular and a spherical form. Figure 3 shows molecular diagrams for two amines and their precursor ammonia. In Fig. 4, four examples of amines in the immobilized form are shown.

More robust pelletized sorbents are being sought to reduce dusting problems. Alternative approaches under investigation are structured sorbent formats such as wash-coated metallic structures and extruded sorbents. Examples of structured sorbents shown in Figure 5 are Microliths®, coated reticulated aluminum foam, and a zeolite honeycomb monolith.

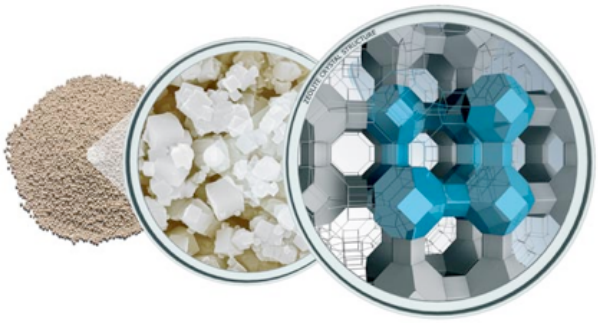

Figure 1. Type A Zeolite. *From right to left, a type A framework structure; zeolite crystals, and zeolite pellets*

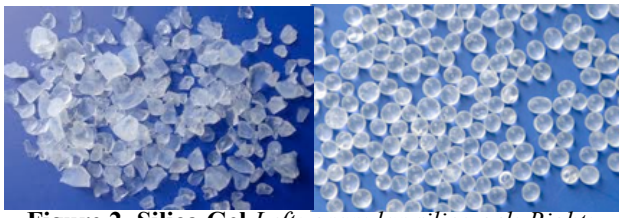

Figure 2. Silica Gel *Left: granular silica gel; Right: beaded silica gel*

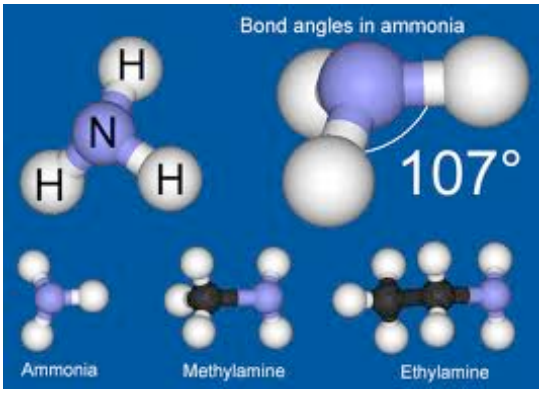

Figure 3. Ammonia and Amine Molecular Structure

Figure 4. Immobilized Amines *Clockwise from upper left: SAMMS (PNNL); SA9T (Hamilton Sundstrand); PEI Silane (NETL); SS61137 (NETL)*

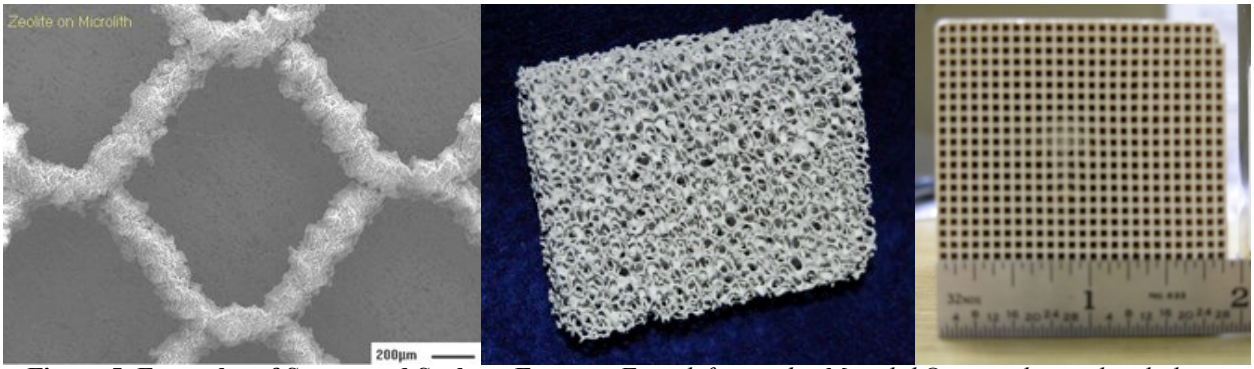

Figure 5. Examples of Structured Sorbent Formats *From left to right: Microlith®, coated reticulated aluminum foam, zeolite honeycomb*

A. Surface Area, Pore Volume, and Pore Size Distribution

Sorbent surface area and pore volume provides an indication of total sorbent capacity. Pore size distribution provides information on the steric separation properties of a sorbent. The sorbent equilibrium capacity taken over a range of sorbate pressures at constant temperature provides the experimental data required for calculation of these parameters. These analyses are being conducted with the Micromeritics TriStar III 3000. Graphical examples of the equilibrium capacity and pore volume are shown in Fig. 7. Sample tabular results are provided in Table 2.

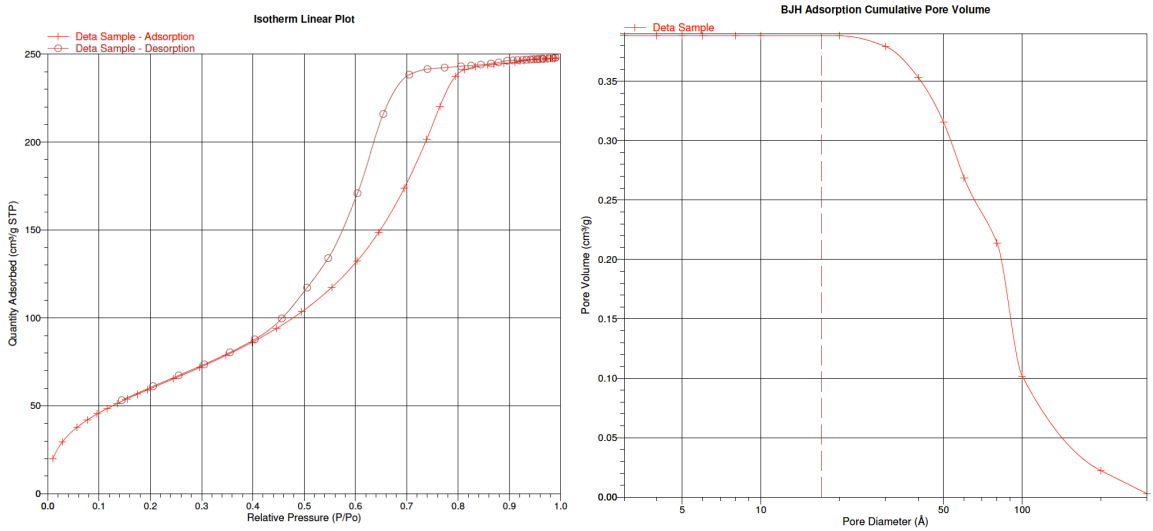

Figure 7. Isotherm Equilibrium Capacity and Cumulative Pore Volume

Table 2. Surface Area, Pore Volume, and Pore Size Analysis

Surface Area	*SAMMS*	*Grace Grade 40 Silica Gel*	*Grace Grade 544 MS 13X*
Single point surface area	207 m2/g	531 m2/g	507 m2/g
BET Surface Area:	236 m2/g	541 m2/g	504 m2/g
Pore Volume			
BJH Adsorption cumulative volume of pores	0.391 cm3/	0.155 cm3/g	0.146 cm3/g
BJH Desorption cumulative volume of pores	0.386 cm3/g	0.173 cm3/g	0.156 cm3/g
Pore Size			
BJH Adsorption average pore diameter (4V/A):	52..6 Å	25.0 Å	135 Å
BJH Desorption average pore diameter (4V/A):	43.8 Å	26.1 Å	105 Å

B. Sorption Kinetics via Thermogravimetric Analysis

Thermogravimetric analysis (TGA) provides a means to measure sorption kinetics, or sorption rates, relatively quickly and/or when only a small amount of sorbent material is available. The pressure swing process (PSA) may be simulated via TGA by holding the furnace at constant temperature and varying the partial pressure of the sorbate in the feed gas. The instrument consists of a microbalance and a glass envelope where the sample may be heated in a controlled atmosphere. Results are given as mass with respect to time, which may be correlated with the temperature program used in the experiment. With conversion of mass to moles of carbon dioxide per kilogram of absorbent the data yields the observed capacity of the absorbent in each cycle.

1. Experimental

The experimental setup used at MSFC is based on that shown in Fig. 8 (Ebner, Gray, Chisholm, Black, Mumford, Nicholson and Ritter 2011). A Perkin Elmer TGA-7 with Pyres software was used in these experiments. Ultra high purity nitrogen gas was passed through a zeolite and indicating desiccant (Dryrite) bed before entering the instrument. A commercially available 1% carbon dioxide gas mixture (Airgas) was used as provided. Absorbents were tested as provided with activation occurring during the experiment.

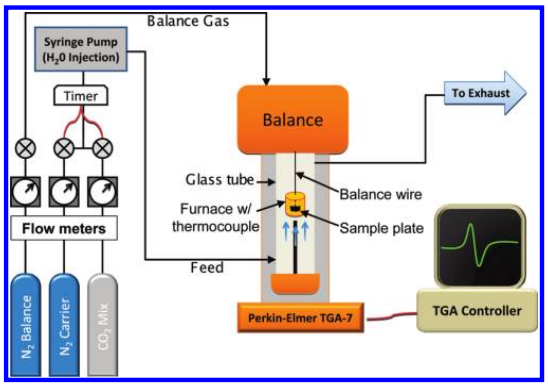

Figure 8. Schematic of the Sorption-Desorption Experimental Apparatus

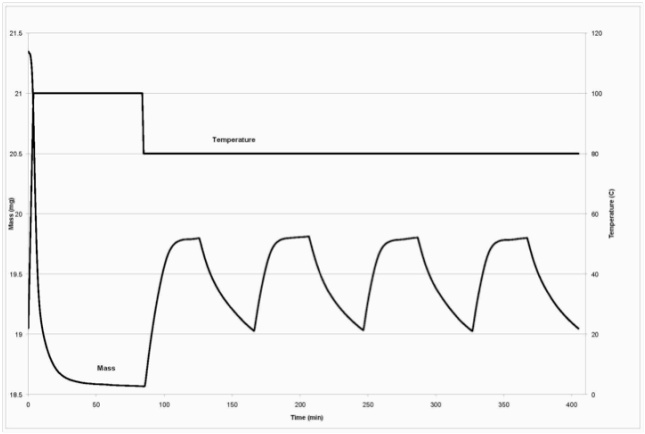

Figure 9. TGA Plot of G-10 Absorbent *Activation followed by cyclic sorption & desorption in dry 1% carbon dioxide at 60 sccm flow rate*

2. Results and Discussion

The results for G10 at 80°C compares well with published values (Ebner, et al. 2011) for adsorption & desorption of 1.2% carbon dioxide on G-10 adsorbent. In our observations, shown in Table 3, SAAMS has a higher capacity than the G-10 absorbent.

C. Pellet Crush Strength Testing

The single pellet crush strength test outlined in the ASTM D 4179 standard provides a straight-forward method of evaluating the ability of a sorbent pellet to withstand the forces exerted on it in a packed bed without fragmenting. This standard was applied to different sorbent types (zeolite and silica gel) and pellet geometries (granular, spherical, and cylindrical) using the apparatus shown in Fig. 10.

Table 3. TGA Analysis Results

Absorbent	Temperature (°C)	Average capacity (moles CO2 / kg absorbent)
G-10	22	0.14
G-10	80	0.93
SAMMS	22	0.25

1. Experimental

Using video capture, we noted that using the maximum load during pellet crushing as the single value of interest (per the standard) failed to capture two key mechanisms: first, the maximum load often occurred following a catastrophic failure, such as the pellet breaking into two or more pieces, and second, dust production occurred for some sorbents at levels much lower than the maximum load or even the load associated with catastrophic failure. Stills from the video capture, with associated load vs. displacement plots, are shown for three sorbents below in Fig. 11-13.

Figure 11 illustrates that significant sorbent failure can occur at much lower loads than the maximum. load. In Fig. 12, dust production occurs initially, then fractures form prior to the maximum load. Finally, in Fig. 13, dust generation and fracturing occurs at loads well below the maximum.

Dust production and sorbent fracturing are undesirable for packed bed applications on long-term mission, as the resulting fines will eventually clog screens and reduce the air flow rate below that required for CO_2 removal. In order to compare candidate sorbents for exploration missions, these mechanisms also need to be evaluated. Additionally, it has been noted that crush strength can differ between activated and humid zeolite pellets. As such, the following additions to the crush strength procedure in ASTM D 4179 have been made:

1. Using video capture correlated with the load vs. displacement graph, observe the mechanisms for pellet failure. Perform this step five times to determine repeatability.
2. Establish a dusting load criteria and a catastrophic event criteria for each sorbent.

3. Perform crush strength test with activated sorbents (to remove moisture) and test with heated platen and dry gas purge.
4. Repeat crush strength test with humidified sorbents (conditioned via flow from humidity generator).

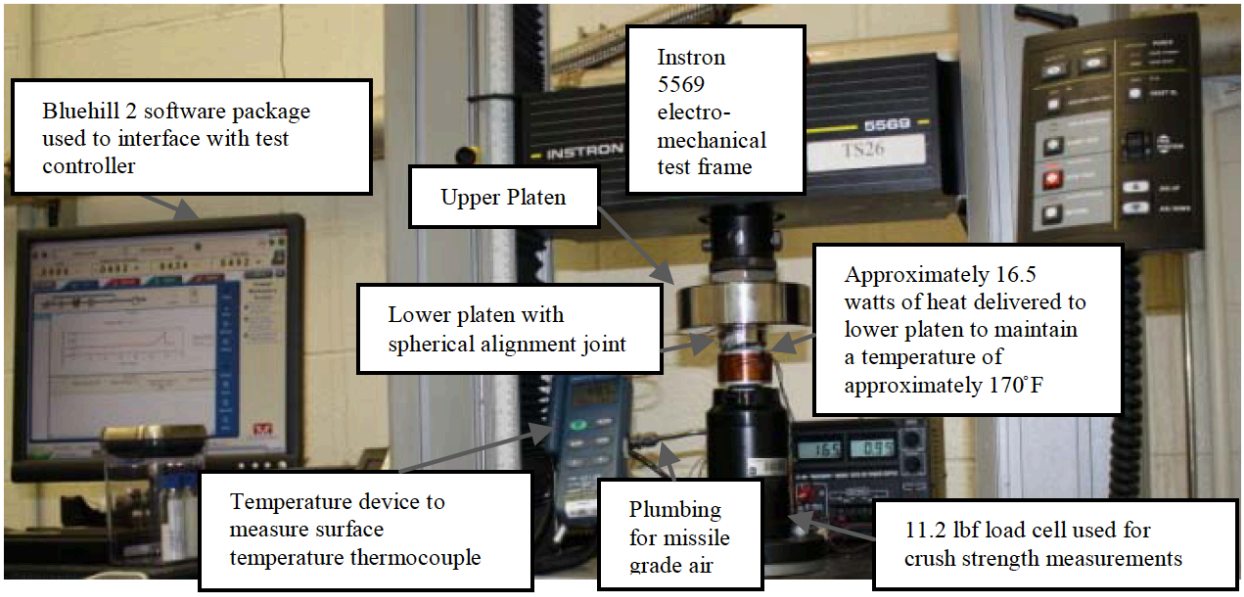

Figure 10. Pellet Crush Strength Apparatus *Reference Standard: ASTM D 4179 Standard Test Method for Single Pellet Crush Strength of Formed Catalyst Shapes; Apparatus: 5569 Electro-Mechanical Test Frame with Bluehill 2 Software*

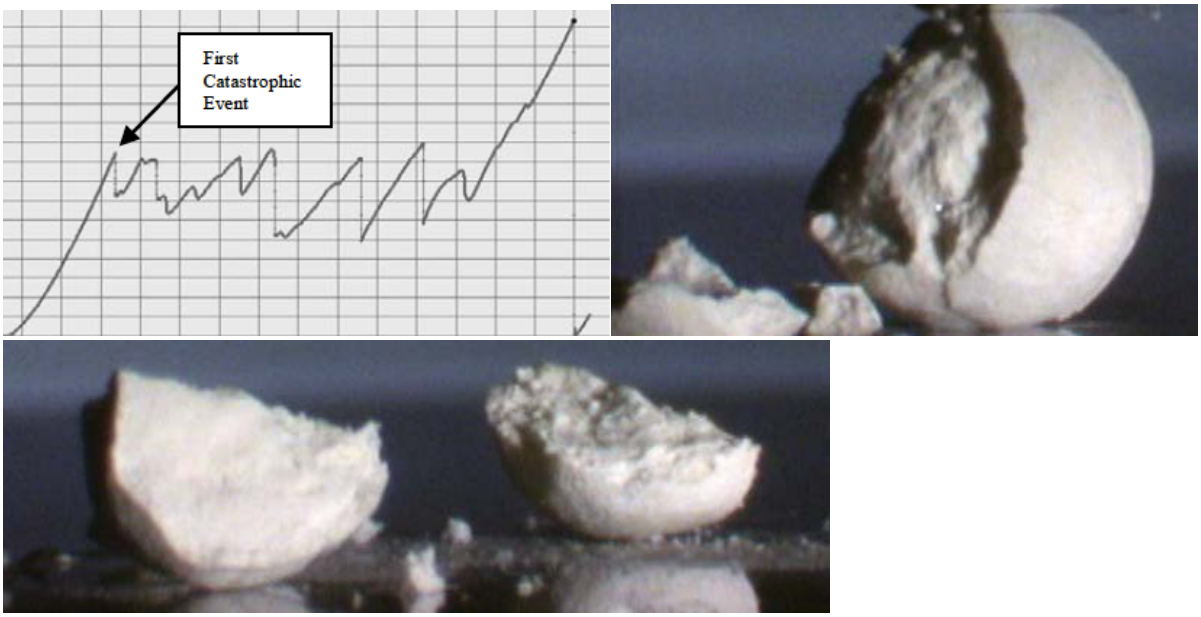

Figure 11. Grace Davison Grade 522 (Zeolite 5A) Crush Testing *Upper left: Load vs. Displacement; Upper right: First catastrophic event; Bottom; after final load drop.*

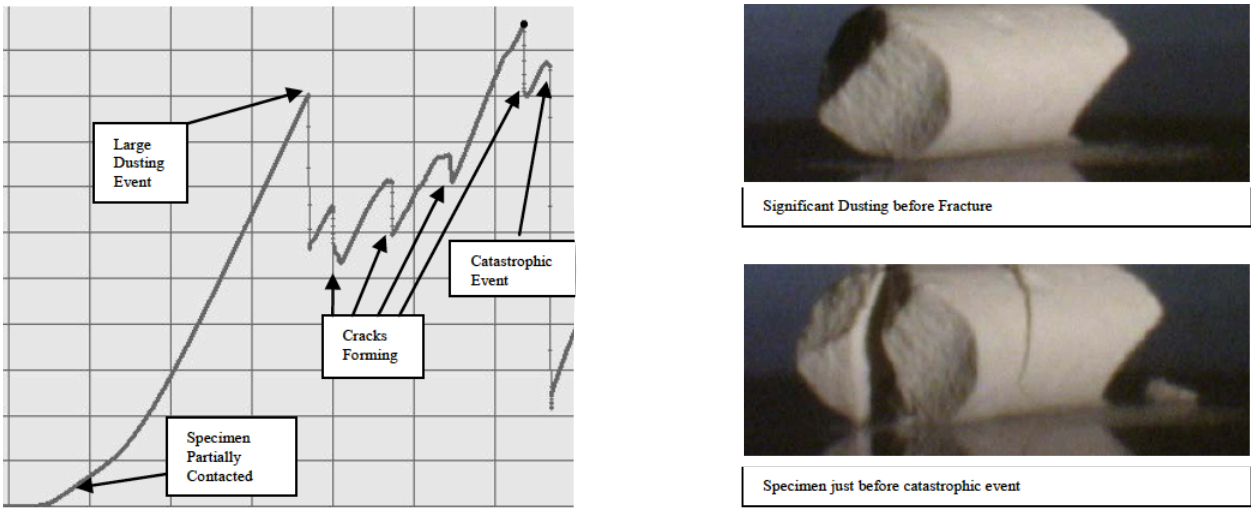

Figure 12. Honeywell ASRT (Zeolite 5A) Crush Testing *Left: Load vs. Displacement; Upper right: Dusting event; Bottom; Specimen just before catastrophic event.*

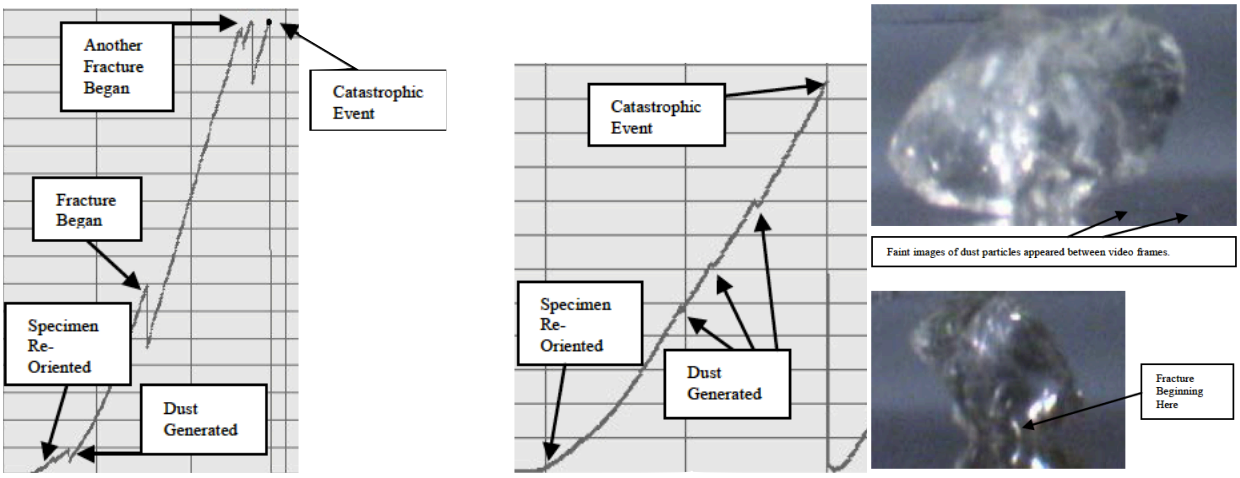

Figure 13. Grace Grade 40 (Silica Gel) Crush Testing *Left: Load vs. Displacement; Upper right: Dusting event; Bottom; Specimen just before catastrophic event.*

2. Results and Discussion

Due to the random nature of pellet crush strength testing results, many pellets must be tested to provide statistically significant results. Sample results are shown for three materials, along with statistical data, in Table 4 below.

Table 5. Pellet Crush Strength Results

Material	# of Tests	Maximum	Minimum	Median	***Mean***	Standard Deviation	Coefficient of Variance
Dusting							
SAMMS	60	1.14	0.002	0.22	***0.31***	0.27	87.69
Grace Grade 40 Room Temperature	53	4.16	0.09	1.15	***1.45***	1.14	78.56
Catastrophic							
SAMMS	60	2.22	0.006	0.65	***0.83***	0.62	74.96
Grace Grade 40 Dry; Room Temp	39	10.22	1.81	3.90	***4.77***	2.42	50.73
Grace Grade 40 Humid; Room Temp	53	10.46	1.03	3.45	***3.69***	1.84	49.88
Grace Grade 522	27	5.88	2.19	4.15	***4.15***	0.99	23.94

D. Packed Bed Breakthrough Testing

Breakthrough tests, where a regenerated column is challenged with a constant inlet of sorbate and carrier gas, are useful both as a direct means to compare sorption kinetics as well as to determine mass transfer coefficients via empirical correlation. The mass transfer coefficient for a sorbate/sorbent pair may then be used to simulate cyclic, regenerative adsorption processes of interest. The development of fixed bed models and verification using breakthrough test results is described elsewhere (Knox, et al. 2012). Here a recently developed low-mass breakthrough test apparatus is described and preliminary results shown.

1. Experimental

A breakthrough test apparatus designed with to have low mass and axial symmetry is shown in Fig. 13. Thin wall aluminum is used to minimize thermal mass. All thermocouples are routed axially. The center section, approximately 5 inches in length, is packed with pelletized sorbent. A schematic of the test stand in also shown in Fig. 13. Mass flow controllers are used to blend nitrogen and CO_2 to the desired partial pressure. Sable Systems CO_2 analyzers provide inlet and outlet percent CO_2 readings. Temperature is measured inside the packed bed at five locations and at the corresponding axial locations on the aluminum skin and on the insulation skin. Absolute and differential pressure is measured in the column inlet and across the column respectively.

2. Results and Discussion

Sample results shown in Fig. 14 illustrate results for CO_2 on two zeolite 5A sorbents and an immobilized amine. The left hand plot is the breakthrough curve for these 3 sorbents. Later breakthrough indicates higher capacity; steeper breakthrough indicates lower mass transfer resistance of the gas from the free stream to the sorbed state. Theoretically, a vertical breakthrough line would be optimal as bed usage would be 100% at breakthrough. In an actual process, sorption and desorption beds are cycled at the time that the partial pressure breaks through a target partial pressure. For bulk sorption, this is about 50% of the inlet partial pressure. For purification processes, the target partial pressure depends on purity requirements. In either case, steeper breakthrough curves permit longer cycles, which, depending on the process, translates to less heating power, less ullage losses, and greater valve life.

The right hand plot in Fig. 14 shows temperatures at the bed center during adsorption. The heat of adsorption may be inferred from this plot, and is clearly higher for the immobilized amine. Heat of adsorption negatively affects adsorption processes, as capacity is reduced at higher temperatures.

Table 6 shows the measured and derived results from these breakthrough tests. Capacity is determined from a mass balance around the packed column. Packed bed differential pressure is also of interest since blower power requirements increases for increased differential pressure.

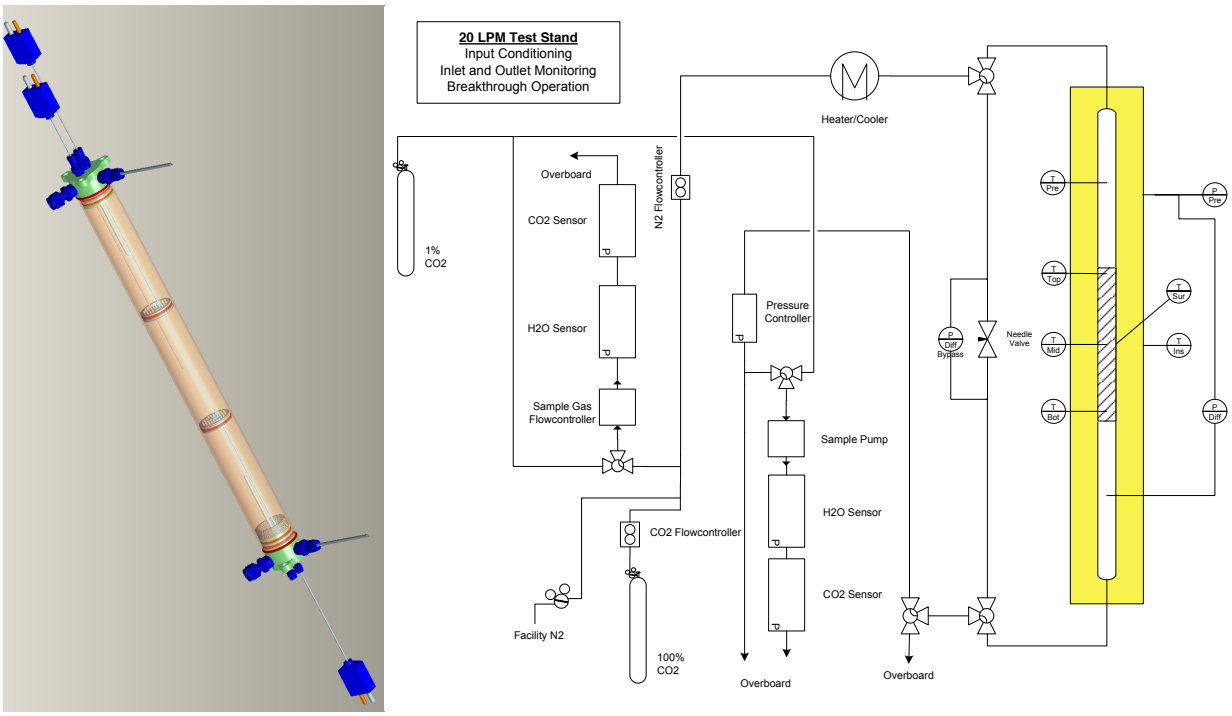

Figure 13. Breakthrough Test Apparatus *Left: Packed bed without insulation; Right: Test stand schematic*

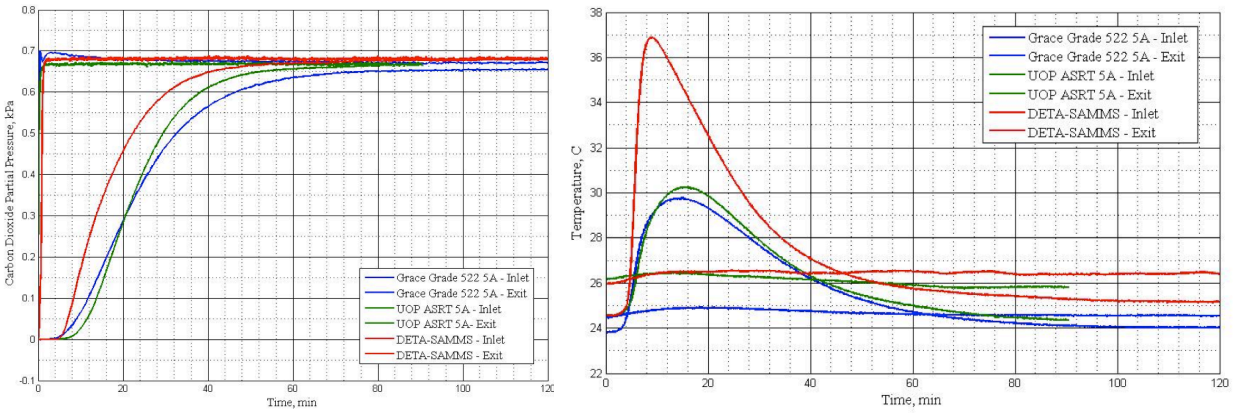

Figure 14. Breakthrough Test Results *Left hand plot: Partial pressure breakthrough; Right hand plot: Temperatures during breakthrough test. Test conditions: 0.69 kPa CO_2, 16 SLPM N_2*

E. Sorbent Characterization and Screening Discussion

As part of the ARREM project, a wide range of sorbent materials will be tested.. Precursor materials such as powders will be assessed for sorbent capacity and kinetics; pelletized and structured sorbent formats will be tested for both performance and durability. Information from these analyses provide the criteria to determine applicability in various sorption processes including

Table 6. Sorbent Capacities and Differential Pressures

Sorbent	Mass [grams]	ΔP Bed [kPa]	Capacity [mol CO2 / kg sorbent]
Grace Grade 522 MS 5A	125	0.7	1.1
UOP ASRT MS 5A	116	0.91	1.01
SAMMS	100	2.21	1.03

CO_2 and H_2O removal.

IV. Sorption Process Development

The description of one sorbent process under development is provided below. The development of other sorption processes, where computer modeling and simulation are the currently the major activity, are discussed in a companion paper (Knox, et al. 2012).

A. Common Atmosphere Revitalization for Exploration (CARE)

The CARE concept is to develop a common adsorption canister for applications ranging from portable life support systems to long-term habitats. The objective is to reduce hardware development costs and increase reliability via long-term testing and operational experience.

Two parallel efforts are being pursued in the development of CARE. The first is a proof of concept (POC) test, where the intent is to characterize the working capacity of a zeolite sorbent as a function of packed bed depth. Figure 15 is the POC test article, showing the pressure transducer locations needed to understand the pressure gradients during desorption. Figure 16 shows the POC test stand schematic.

The second effort is the conceptual design of a flight system, as shown in Figure 17. Features of this design are:

- Modular rotating valve design with Parker Gask-O-Seals integral to the bed.
- High vacuum conductance with large window area exposed to vacuum.
- Compact design with few moving parts.

Although the final design dimensions will be guided by data from the POC testing, an initial conceptual design provides an understanding of any technology development needs. For example, the use of Parker Gask-O-Seals must be verified for this application. Specifically, these seals must be tested for tolerance to temperatures used for desorption and potential abrasion during travel across the window area.

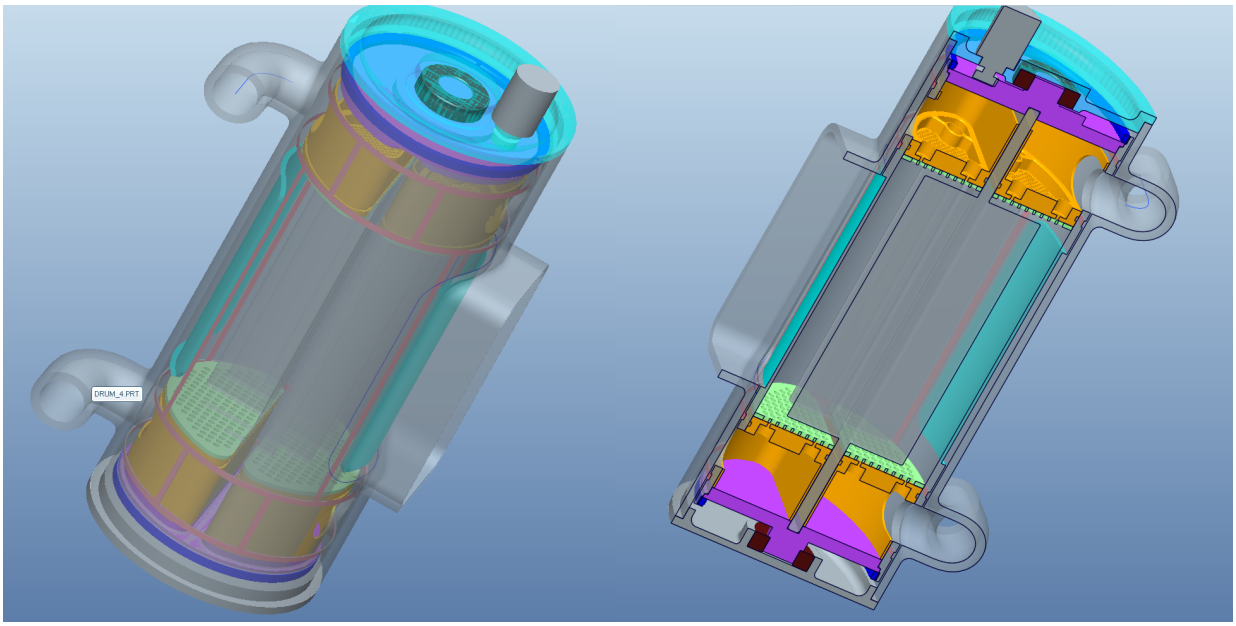

Figure 17. Conceptual Flight Design for CARE

V. Conclusions

The need for atmosphere revitalization systems that are optimized with respect to performance, resources, and is necessitated by the aggressive new missions planned by NASA. With NASA budgets remaining flat, innovative approaches to new system development are required. This paper presents such an approach for the AES ARREM project, where testing is supplemented with modeling and simulation to reduce costs and optimize hardware designs. In this paper, we have also discussed a sorbent screening and characterization approach intended to select high per-

formance, durable sorbents to be applied to exploration life support systems and a novel concept for commonality in sorbent canister designs.

The efforts represented here will be continued to support the design of Atmosphere Revitalization systems under the ARREM project. These modeling and simulation efforts are expected to provide design guidance, system optimization, and troubleshooting capabilities for atmosphere revitalization systems being considered for use in future exploration vehicles.

VI. References

1 **NASA**. Human Exploration & Operations (HEO). 2012).

2 **Knox, J.C., Coker, R.F., Kittredge, K., Cummings, R. and Gomez, C.F.** Developments in Atmosphere Revitalization Modeling and Simulation. *Interational Conference on Environmental Systems* (AIAA, San Diego, 2012).

3 **Perry, J.L., Abney, M.B., Knox, J.C., Parrish, K.J. and Roman, M.C.** Integrated Atmosphere Resource Recovery and Environmental Monitoring Technology Demonstration for Deep Space Exploration. *International Conference on Environmental Systems* (AIAA, San Diego, 2012).

4 **El Sherif, D. and Knox, J.C.** International Space Station Carbon Dioxide Removal Assembly (ISS CDRA) Concepts and Advancements. *International Conference on Environmental Systems* (SAE, Rome, Italy, 2005).

5 **Ebner, A.D., Gray, M.L., Chisholm, N.G., Black, Q.T., Mumford, D.D., Nicholson, M.A. and Ritter, J.A.** Suitability of a Solid Amine Sorbent for CO2 Capture by Pressure Swing Adsorption. *Ind. Eng. Chem. Res.*, 2011(50), 5634-5641.