

Development of Carbon Dioxide Removal Systems for NASA's Deep Space Human Exploration Missions 2017-2018

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NASA has embarked on an endeavor that will enable humans to explore deep space, with the ultimate goal of sending humans to Mars. This journey will require significant developments in a wide range of technical areas, as resupply is unavailable in the Mars transit phase and early return is not possible. Additionally, mass, power, volume, and other resources must be minimized for all subsystems to reduce propulsion needs. Among the critical areas identified for development are life support systems, which will require increases in reliability and reductions in resources. This paper discusses current and planned developments in the area of carbon dioxide removal to support crewed Mars-class missions.

I. Nomenclature

<i>AES</i>	=	Advanced Exploration Systems
<i>ACLS</i>	=	Advanced Closed-Loop System
<i>AC-TSAC</i>	=	Air Cooled Temperature Swing Adsorption Compressor
<i>ARC</i>	=	Ames Research Center
<i>ARREM</i>	=	Atmosphere Revitalization Recovery and Environmental Monitoring
<i>BET</i>	=	Brunauer–Emmett–Teller
<i>CASIS</i>	=	Center for the Advancement of Science in Space
<i>CDRA</i>	=	Carbon Dioxide Removal Assembly
<i>CDRILS</i>	=	Carbon Dioxide Removal by Ionic Liquid Sorbent
<i>CnD</i>	=	Countercurrent Depressurization Step
<i>CRCS</i>	=	Carbon Dioxide Removal Compression and Storage
<i>CO₂</i>	=	Carbon Dioxide
<i>ECLSS</i>	=	Environmental Control and Life Support System
<i>EPSCoR</i>	=	Experimental Program to Stimulate Competitive Research
<i>FOM</i>	=	Figure of Merit
<i>ISS</i>	=	International Space Station
<i>JAXA</i>	=	Japan Aerospace Exploration Agency
<i>LDST</i>	=	Long Duration Sorbent Testbed
<i>LSSP</i>	=	Life Support Systems Project
<i>NETL</i>	=	National Energy Technology Laboratory
<i>MSFC</i>	=	Marshall Space Flight Center
<i>MOF</i>	=	Metal-Organic Frameworks
<i>N₂</i>	=	Nitrogen
<i>NAVSEA</i>	=	U.S. Naval Sea Systems Command
<i>NASA</i>	=	National Aeronautics and Space Administration
<i>NRA</i>	=	NASA Research Announcement
<i>O₂</i>	=	Oxygen
<i>PSA</i>	=	Pressure Swing Adsorption
<i>PTSA</i>	=	Pressure and Temperature Swing Adsorption
<i>PNNL</i>	=	Pacific Northwest National Laboratory
<i>SAA</i>	=	Space Act Agreement
<i>SBIR</i>	=	Small Business Innovative Research
<i>SMT</i>	=	Systems Maturation Team

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TC-TSAC = Thermally Coupled Temperature Swing Adsorption Compressor
TIM = Technical Interchange Meeting
TRL = Technology Readiness Level
TSA = Temperature Swing Adsorption
TVSA = Temperature/Vacuum Swing Adsorption

II. 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, Phase 0, “*Earth Reliant exploration is focused on research aboard the ISS. On the space 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.*”

In this paper, NASA-sponsored efforts to develop CO₂ Removal technologies (part of a life support system) for Exploration missions are described. In general, the goal of these efforts is to develop an International Space Station (ISS) flight demonstration. Here the ISS will provide the platform for long-term system testing in a relevant environment, thus enabling the evaluation and certification of the technology candidates for future spacecraft. In addition, NASA-funded work underway on sorbents and systems at lower technology readiness levels (TRLs) are discussed. These development efforts have the potential to be applied as upgrades to existing systems, as merited, or to future surface habitats.

The objective of this paper is to outline the current NASA-funded efforts in CO₂ removal systems and material development in the context of the NASA CO₂ Removal Roadmap. References are provided to enable review of the detailed works on each development effort.

III. Background

It is recognized by the life support community that the current ISS state-of-the-art CO₂ removal technology has reliability and capability gaps that must be solved both for ISS and future Exploration missions. From Fiscal Year 2012 (FY12) to FY14, the Atmosphere Revitalization Recovery and Environmental Monitoring (ARREM) project under the Advanced Exploration Systems (AES) program included efforts to improve the CO₂ Removal state-of-the-art by seeking more robust sorbents and evaluating alternate sorbent formats and fixed-bed configurations²⁻⁴. This scope was broadened when, in early 2014, the ISS Program Manager requested that the NASA Environmental Control and Life Support System (ECLSS) Systems Maturation Team (SMT) review all possible alternate technologies and provide a recommendation to the ISS Program to guide decisions relative to next steps for CO₂ removal. This recommendation was to include goals for both ISS and future Exploration missions.

As reported on in a previous paper⁵, technical interchange meetings (TIMs) were held in the spring of 2014 to determine criteria and goals for Exploration CO₂ removal systems and gather information on the state-of-the-art of CO₂ removal technologies in the defense, environmental, commercial and academic sectors. The information gathered at these TIMs was used to develop a proposed roadmap, the current version of which is shown in Figure 1. The near-term goal is to develop flight demonstrations to be flown on the ISS for an extended period of time as required to assess long-term performance and reliability in a relevant environment. Following testing of the individual CO₂ removal technologies, one will be selected for an integrated air string that will be tested for a minimum of three years as part of the Phase 0 Exploration ECLSS Integrated Demonstration.

NASA CO₂ removal technology development has continued under the AES Life Support System Program (LSSP) and the ISS Exploration office from FY15 to FY18⁶⁻⁷. In the following sections, the details of the current approach and a summary of recent work are presented.

IV. Carbon Dioxide Removal Roadmap

The CO₂ Removal Roadmap shown in Figure 1 provides a high-level overview of the current and planned NASA-sponsored efforts in the area of closed-loop spacecraft carbon dioxide removal. Closed-loop in this context refers to capture of CO₂ for the purpose of downstream processing. An example of downstream processing is the Sabatier reactor used on ISS to reduce CO₂ in the presence of H₂ (a byproduct of electrolysis used in O₂ production) to produce water. The water produced by this process is used by the crew, reducing the water quantity that must be transported

to the ISS from earth. Maximizing recycling, or more fully closing the loop, becomes even more critical on manned missions with infrequent or non-existent resupply opportunities, such as the Mars transport class of missions.

The CO₂ Removal Roadmap consists of three primary sections. The uppermost band (blue background) describes current and planned on-orbit operations of experiments and technology demonstrations with relevance to exploration CO₂ removal systems. The largest section is in the center of the roadmap (white background), and contains the milestones, decision points, and activities both underway and planned in the area of closed-loop CO₂ removal. This section is further divided, with the top section showing technologies that are expected to be evaluated as part of the individual CO₂ removal technology demonstrations on the ISS. The bottom section (enclosed by a blue border) includes lower TRL technologies that have potential for future upgrades for transit spacecraft and/or surface habitats. The band (green background) near the bottom of the roadmap provides a reference for the activities relevant to the current ISS CO₂ removal system, the Carbon Dioxide Removal Assembly (CDRA). Finally, text is provided at the bottom of the roadmap with the high-level objectives and Figures of Merit for Mars-class missions.

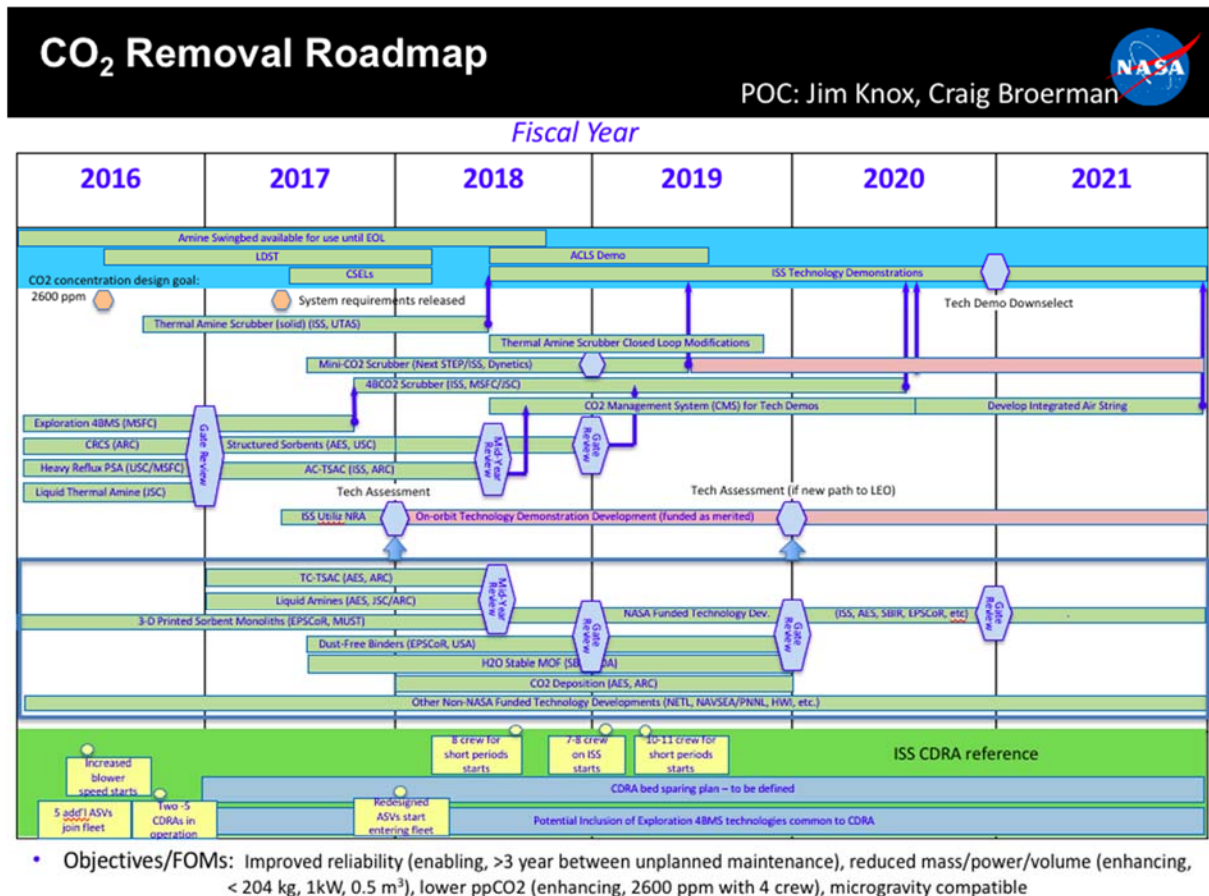


Figure 1. Carbon Dioxide Removal Roadmap

V. On-Orbit Operations

The top-most blue band in the roadmap shows current and planned CO₂ removal activities on the ISS. Each of the activities are discussed below. The individual technologies being developed for on-orbit technology demonstrations in the center section of the roadmap will be discussed in some detail following a summary of near-term on-orbit activities.

A. Amine Swingbed

The Amine Swingbed is an open-loop CO₂ removal technology⁸ currently on-orbit that operates in a Pressure Swing Absorption (PSA) cycle. CO₂ and a small amount of water is absorbed at atmospheric pressure and desorbed

at reduced pressure to space. However, it is included on this roadmap because it uses a solid amine (SA9T) sorbent that is being considered for use in a future, more fully closed-loop flight technology demonstration, the Thermal Amine Scrubber. The Amine Swingbed has already achieved its experimental objectives of 1000 hours of operation. It has been used to augment the primary CO₂ removal systems, the U.S. CDRA⁹ and Russian Vozdukh systems. However, due to the water loss to space during vacuum regeneration of the amine absorbent, this system is currently used only when required due to a large ISS crew or during repair of the primary CO₂ removal systems.

B. Long Duration Sorbent Testbed

The Long Duration Sorbent Testbed (LDST)¹⁰ is a flight experiment demonstration designed to expose current and future candidate carbon dioxide removal system sorbents to an actual crewed space cabin environment to assess sorption working capacity degradation resulting from long term operation. The need for this experiment was realized after an analysis of sorbent materials returned to Earth after approximately one year of operation in the International Space Station's Carbon Dioxide Removal Assembly. These analyses indicated as much as a 70% loss of working capacity of the silica gel desiccant material at the system inlet location, with decreasing capacity loss for samples deeper in the bed. The primary science objective is to assess the degradation of potential sorbents for Mars-class missions and ISS upgrades when operated in a true crewed space cabin environment.

The LDST flight experiment operated for one-year in the ISS and was returned to earth in November 2107. The experiment consisted of two small scale CDRA-like loops, with one loop consisting of sorbents previously flown in the CDRA and the other loop consisting of sorbents under consideration for use in future missions. The second loop shut down due to a high differential pressure fault. As of this writing, the disassembly and evaluation of the flight unit are underway and will determine the cause of the fault and analyze the sorbents for degradation resulting from the extended exposure to the ISS atmosphere.

C. Advanced Closed-Loop System

The Advanced Closed-Loop System (ACLS)¹¹ is a regenerative life support system for closed habitats developed under funding from the European Space Agency. Using regenerative processes, the ACLS includes the life support functions of CO₂ removal, oxygen generation and CO₂ reprocessing. After many years of predevelopment, the ACLS project started into flight development in 2011.

Recently, the ACLS Flight Model (FM) hardware passed environmental testing, safety testing, interface testing and final performance testing. Shipment to JAXA, the launch service provider, was underway at this writing. Launch of the ACLS FM is planned for August 2018 on HTV7. Please refer to reference 11 for further information.

D. Capillary Structures for Exploration Life Support (CSELS)

The Capillary Structures for Exploration Life Support flight experiment¹² flew in 2017 to evaluate ECLSS technologies that utilize potentially game changing capillary structures for fluid containment and management, including a proof-of-concept test for carbon dioxide removal using liquid sorbents. This flight experiment had three technical goals:

- Demonstrate functional performance of long duration processes
- Demonstrate capillary structures as a valid form of fluid containment
- Provide data for validation of microgravity fluidics models and terrestrial evaluation techniques

The flight experiment will provide guidance for the further development of capillary structures the area of CO₂ removal. Test results will indicate feasibility of this approach and help determine the appropriate direction for design improvements and further testing.

VI. Carbon Dioxide Removal Requirements

The development of a consistent set of CO₂ removal requirements is important to provide the basis for the gate reviews and technology assessments shown on the CO₂ Removal Roadmap. The importance of one specific requirement, cabin CO₂ partial pressure, is such that it required a dedicated forum in FY16¹³⁻¹⁵. The result of this forum was to specify a cabin partial pressure of 2 torr as the design goal for technology development. This level is pending medical studies to further understand the combined influences of CO₂ partial pressure and microgravity on human physiology. In FY17, the overall CO₂ removal requirements were refined to provide guidelines for technology assessments¹⁶.

VII. CO₂ Removal Development Efforts toward On-orbit ISS Technology Demonstrations

The primary near-term goal of the NASA CO₂ removal effort is to take advantage of the ISS as the optimal Mars mission class technology testing laboratory. The ISS environment includes both micro-gravity and an atmosphere that is unique to a long-duration spacecraft. Micro-gravity is critical to understanding particulate and liquid behavior in this environment. The spacecraft atmosphere has higher concentrations of many trace gases than on Earth, a result of a spacecraft being a tightly sealed system. Successful testing of potential Mars-class mission systems on the ISS provides a high degree of confidence of success for an actual Mars mission, which is critical for this mission when no opportunity exists for either emergency resupply or a rapid return to Earth.

As shown in Figure 1, the on-orbit ISS technology demonstrations for potential NASA Mars-class mission CO₂ removal technologies are planned to begin in the middle of fiscal year (FY) 2018.

A. Thermal Amine Scrubber

The permanent number of crew on the ISS will be increased to as many as eight in early FY18 as shown in the “ISS CDRA reference” section of the CO₂ Removal Roadmap. In addition, increases in the number of crew to eight for short periods will begin in FY18. Increases to up to eleven crew for short periods will begin in early FY19. To provide additional CO₂ removal capability for these crew increases the Thermal Amine Scrubber is being funded as an early flight technology demonstration project by the ISS program, as well as to provide operational experience to help assess applicability of this technology for exploration missions. Launch of this system to the ISS is planned for June of 2018. This flight system bears many similarities to that described in the work of Papale et al¹⁷ especially with respect to the desiccant and sorbent bed hardware and materials, although the packaging has been adapted to fit in an EXPRESS rack instead of an Atmosphere Revitalization rack. Also, the current flight system will be configured for open loop mode only, such that a follow-on effort will be required for closed loop modifications.

B. Mini-CO₂ Scrubber

The miniature CO₂ scrubbing system will demonstrate a new, highly efficient system that removes carbon dioxide and potentially other undesirable gases from spacecraft cabin air¹⁸⁻¹⁹. The core of this system is the Scrubber Cartridge System (SCS), a microfluidic separation unit implemented in a wafer produced using microfabrication techniques. The wafer design has undergone multiple design iterations; currently the sixth-generation wafer design is underway. One or more wafers will be encapsulated in a removable cartridge. A conceptual design of a cartridge is shown in Figure 2. The overall system including balance of plant components (valves, compressor, sensors, etc.) will be implemented in an EXPRESS rack double locker, also shown in Figure 2. The hardware is planned for delivery in June of 2019.

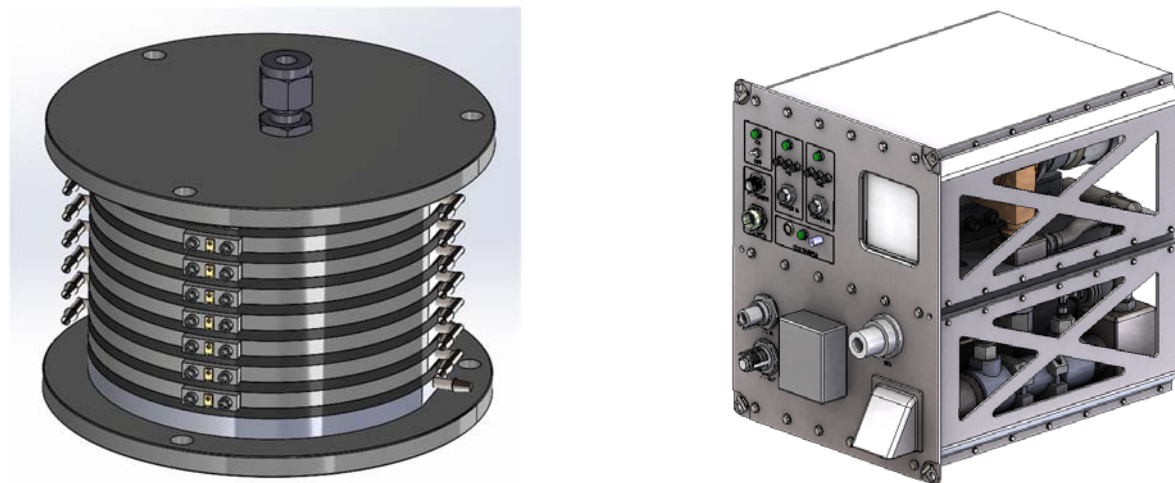


Figure 2. Mini-CO₂ Scrubber; cartridge concept (left) and overall configuration (right)

C. 4-Bed CO₂ Scrubber

After a number of years as a development project,²⁰⁻²¹ the 4-Bed CO₂ Scrubber (4BCS) was funded as a flight demonstration project by the ISS program. Authority to proceed was granted on August 1, 2017. A conceptual drawing, along with design improvements, of the 4BCS are shown in Figure 3. Supporting efforts in understanding

the fundamentals of 4BCS sorbent behavior are described next, followed by an investigation of structured sorbents as a potential replacement for the pelletized sorbents baselined for the 4BCS system.

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

An oversized residual desiccant layer has been found to reduce overall system performance²². An optimal zeolite 13X layer can improve system performance by 50% and proof of concept testing has already shown 20% improvement. 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 CO₂ and H₂O is significant due to the non-linear behavior. Water is adsorbed in significant amounts at concentrations of 1 ppm while CO₂ is adsorbed in similar quantities at 1000ppm concentrations. Additionally, adsorption of traces of water vapor has a significant impact on CO₂ adsorption, but quantifying the amount of water adsorbed is very challenging. Some works have attempted to measure the co-adsorption behavior directly while others have measured the behavior of a packed bed. The material studied here is a commercially available 13X zeolite which is to be used in the next generation 4BMS system.

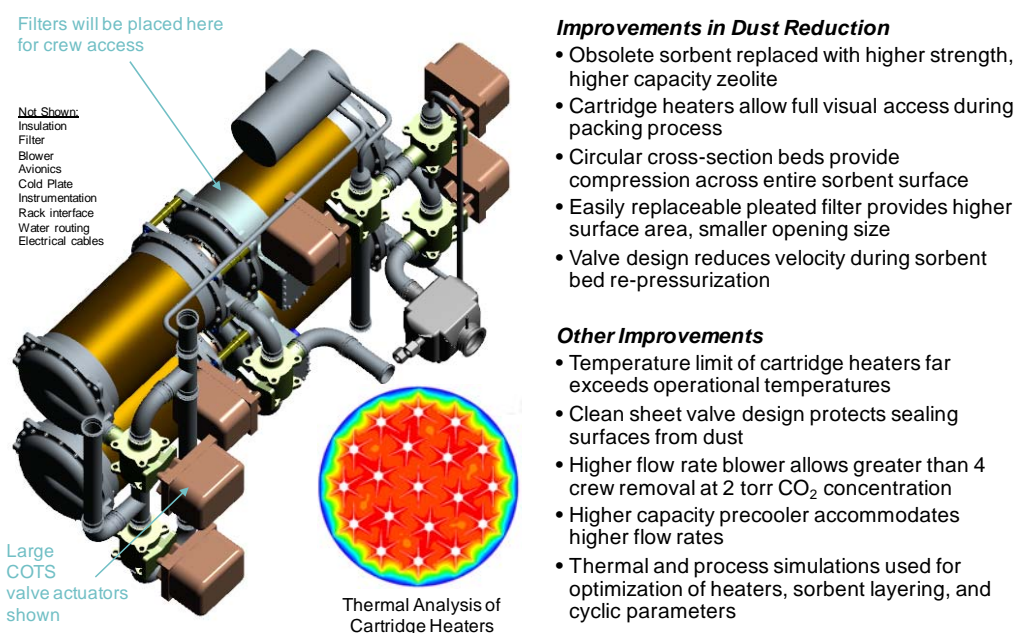


Figure 3. 4-Bed CO₂ Scrubber Concept

A representative set of results obtained are shown in Figure 4. In addition, reference isotherms are provided of both dry, pure component CO₂ measurements²³ and a set of similar water preloaded measurements. Further measurements were conducted at 50°C, 75°C, 100°C, and 175°C.

The measurements were used to fit a proposed model for CO₂ adsorption in the presence of a quantity of preloaded water. The new model adds two parameters to an existing CO₂ isotherm fit to pure, dry isotherm measurements.

The proposed and fit model is to be used in a simulation of a full-scale CO₂ removal system for future crewed missions. Optimization with a well-informed simulation can improve the overall removal performance. For further information refer to the work of Cmarik and Knox²².

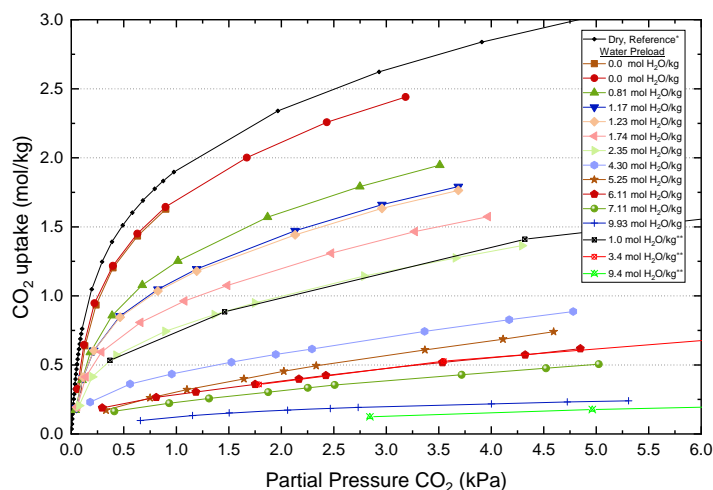


Figure 4. CO₂ isotherms measured on zeolite 13X at a number of water preloadings

2. Analysis of Performance Degradation of Silica Gels after Extended Use Onboard the ISS

Samples from bed teardowns from units used in CDRA-3 and CDRA-4 revealed significant discoloration of the silica gel near the bed inlet as well as a coincidental performance loss²⁴⁻²⁵. This material was analyzed for the presence of chemical contaminants, physical porosity changes, and adsorption performance. The material characteristics are compared against the location in the bed from which they were sampled in order to develop profiles through the bed. Additional testing of the beds prior to teardown provided more data points. Possible mechanisms for the loss of capacity are provided though no root cause has been found. Extrapolation of the performance loss is used to estimate the required oversizing of the silica gel layer for long-term operation.

Chemical composition analysis results from the CDRA-3 samples showed a correlation between siloxane content and loss of performance. Other correlations were noted between excess metal content and performance loss. The chemical composition analysis results from the CDRA-4 samples shows no correlation between siloxane nor metal content and loss of performance. There was no detectable siloxane content on all of the CDRA-4 samples except for a small amount on the Sorbead WS material from one desiccant bed. Surface area and pore volume analysis via the BET method showed a consistent trend across sample depth.

In order to probe the effects of adsorbed contaminants in the materials, water vapor isotherms were measured on the available materials. Surface area correlates strongly with capacity. The samples taken from the end of the desiccant bed closest to the cabin air inlet show the greatest loss of performance, while samples taken from positions that correspond to drier sections of the bed which also see hotter temperatures are more similar to control samples. All flight samples show at least a slight reduction in performance against control samples. At high capacities, a nearly linear extrapolation from lower water vapor concentration results is observed. As shown in Figure 5, the front of the bed is severely degraded by almost 50% from the control sample while the remainder of the bed shows a 15% to 25% reduction in capacity. This capacity loss may be significant to system operation.

An alternative degradation mechanism is proposed. During desorption cycles of a desiccant bed, a water vapor concentration wave and a hot temperature wave are observed in test and computer simulation. These thermal and concentration waves progress through the bed at different rates with the concentration wave preceding the hot purge wave. This cycles the front layer of silica gel through its entire capacity range during each CDRA cycle. Broken SGB125 beads are observed in the sample vials consistent with exposure to liquid water droplets as observed in controlled misting tests. No sub-scale tests have successfully replicated the discoloration. Sorbead WS is also found to be severely degraded, despite its stability against misting and high pellet strength. The 13X zeolite used in the flight beds was found to be indistinguishable from control samples.

A conservative threshold for drying failure, defined as detectable breakthrough of water vapor, was estimated to occur when the silica gel layer of a CDRA-4 desiccant bed was reduced to 55% of original capacity. Four possible mechanisms are postulated from test data. The estimated additional mass of silica gel required to compensate for losses range from no additional mass needed to more than doubling the present amount. Certainly, more efforts are needed to understand the causes and mitigate risks for long-duration missions. For further information refer to the work of Cmarik et al²⁴.

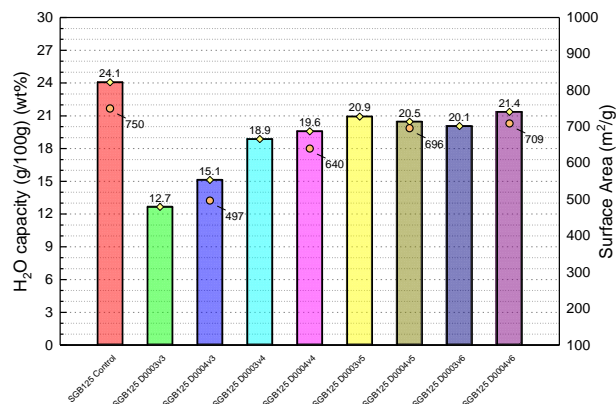


Figure 5. Results of one water vapor adsorption test at high concentrations which closely match the inlet concentration for CDRA. Adsorption was conducted at 25°C and interpolated at 12,500 ppmv. The first bar represents a control sample, while the subsequent bars represent samples taken at increasing distances from the front of the bed.

3. PTSA Process with a Structured Sorbent

A CatacelTM, parallel channel, metal foil structured sorbent is being evaluated for direct replacement of the pelletized zeolite in the 4BCS CO₂ sorbent beds because pelletized zeolites have experienced dusting issues and associated equipment problems. The Catacel structured 13X sorbent column is shown in Figure 6(a). This column mimicked the 4BCS CO₂ PTSA cycle by heating with eight band heaters and by cooling with ambient air blown across the column axially during the TSA dynamic cycling experiment.

The 2-bed cycle schedule used in this PTSA single bed apparatus is not meant to be a prototypic cycle, as it is limited by its unique heat up and cool down characteristics provided by the external band heaters and axial air blowers. It is also limited by its vacuum capability. Nevertheless, it is close to the actual 4BCS CO₂ cycle operation and used to show whether the Catacel structured 13X column can provide the same performance of the existing 4BCS CO₂ PTSA system.

The PTSA cycle consisted of pressurization with feed for 8 s, feed at 14.8 psia for 4,792 s, air save down to 1.5 psia for 600 s and countercurrent depressurization down to 0.4 psia for 4,200 s. The feed flow rate of N₂ was 7.1 SLPM and that for CO₂ was 0.0187 SLPM, which when blended provided a CO₂ feed concentration of 2,634 ppm. The Catacel structured 13X column contained 75 g of zeolite. Knowing the amount of zeolite in this bench scale column and that in the 4BMS-X, allowed the feed flow rate to be scaled down from the full-scale value.

A single PTSA 1-bed run with the Catacel structured column was carried out. The resulting temperature, pressure and CO₂ concentration histories over three and one-half cycles are shown in Figure 6(b). The heat up and cool down set points were 170°C and 5°C. T1 to T8 are on the surface of the column from bottom to top, and Axial T is in the middle of the column both radially and axially. The temperatures were uniform along the length of the column. The pressure histories during the feed (15 psia), CnD Air Save (transient down to 1.5 psia) and CnD Vacuum steps (transient down to 0.4 psia) were also uniform over the cycles. The CO₂ concentration in the light product during the feed step and heavy product during the vacuum step showed that a very high purity product was produced.

Several positive conclusions were drawn from this preliminary TSA single bed run with a Catacel structured column. This preliminary run came very close to providing the required CO₂ removal rate of 4.0 kg/day, while provided a very high purity CO₂ product. 3.84 kg/day of CO₂ were removed, while using a high temperature of 170°C, a low pressure of only 0.4 psia and a rather slow cool down rate. The slower cool down rate would have caused more CO₂ to breakthrough and be lost in the light product. This could easily be improved and would not be a limitation on a properly designed full scale 4BMS-X utilizing a Catacel structured column. The higher than prototypic low pressure would also cause less regeneration of CO₂ and thus less CO₂ in the heavy product. This could easily be improved with a better vacuum pump system and would not be a limitation on a full scale 4BMS-X utilizing a Catacel structured column. The lower than prototypic high temperature would also cause less regeneration of CO₂ and thus less CO₂ in the heavy product. This could easily be changed and would not be a limitation on a full scale 4BMS-X utilizing a Catacel structured column. This non-prototypic operation will be modified and more prototypic operations will be tested in future runs. Over all, these results indicated a drop-in replacement with a Catacel structured sorbent may be possible. Continued testing will confirm if this is the case.

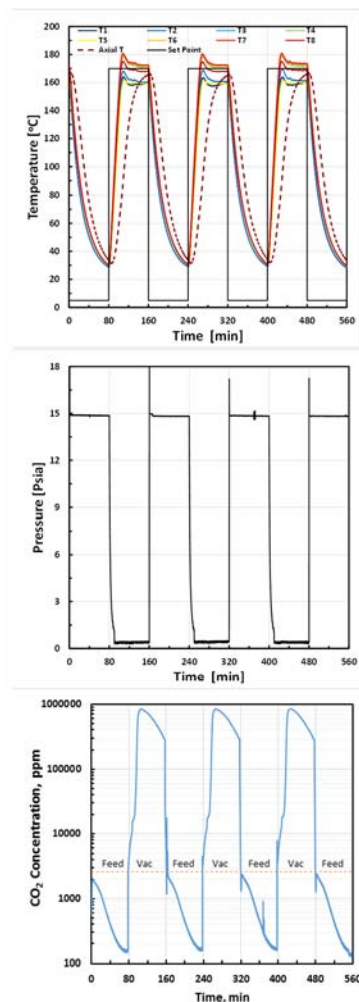
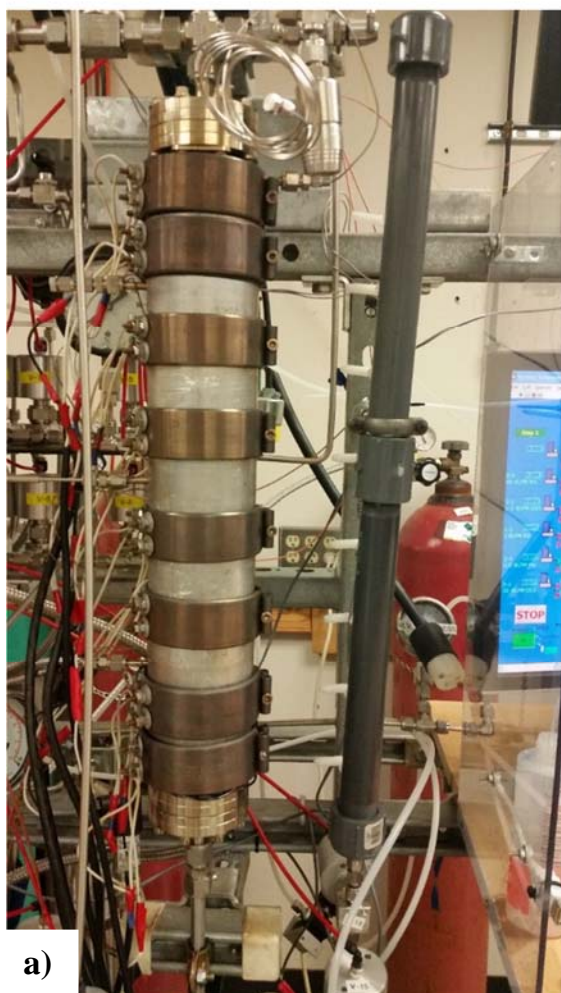


Figure 6: (a) PTSA single bed structured column. (b) Temperature, pressure and CO₂ concentration histories over three and one-half cycles. The feed concentration of 2,634 ppm CO₂ is indicated by the red-dashed line

Temperature Swing Adsorption Compressors (TSACs) capture and store sorbates in high surface area, high capacity sorbents. The compression stage consists of heating and isolating the fixed bed until the sorbate in the gas phase reaches the desired delivery pressure, then supplying the sorbate gas to the downstream component (for example, a Sabatier reactor). The TSAC replaces the functions of two current components, the mechanical compressor and the accumulator. Two versions of the TSAC are under consideration for future air revitalization systems: The Air-Cooled TSAC (AC-TSAC) and the Thermally- Coupled TSAC (TC-TSAC). These will be discussed in the following sections.

E. Air-Cooled Temperature Swing Adsorption Compressor

The AC-TSAC consists of two independent fixed beds of zeolite 5A, each with embedded heaters for operation up to 300°C. The two beds alternate between adsorption and production phases, enabling the constant production of CO₂ to a downstream CO₂ reduction system. This technology has been previously tested in an integrated configuration with a development of the 4BMS system²⁶. The AC-TSAC is a stand-alone system that will not be tightly integrated with the 4BMS-X design in operation, which allows for an independent parallel design path.

The TSAC approach was shown to trade favorably against the combination of a mechanical compressor and accumulator with respect to mass in the analyses presented at the FY16 Gate Review. In FY17, long-term testing of the AC-TSAC hardware used in the 2006 integrated test at MSFC was completed and leaks in the canister lids prevented further testing. Currently, a trade study of the TSAC vs. a mechanical compressor and accumulator is being conducted. Pending trade study results, the AC-TSAC hardware will be redesigned and fabricated as needed. Please refer to the work of Richardson and Jan²⁷.

VIII. Lower TRL CO₂ Removal Development Efforts

A. Thermally Coupled Temperature Swing Adsorption Compressor (TC-TSAC)

The Carbon Dioxide Removal and Compression System (CRCS) consisted of two concentric cylinders: the CO₂ removal function (stage 1) is located in the inner annulus; and the CO₂ compressor function (stage 2) is located in the outer cylinder²⁸. This design is an improvement on the AC-TSAC by attempting to lower the power input during thermal regeneration. The shared wall between stage 1 and stage 2 allow for the heat generated in stage 1 to be used by stage 2. During integrated testing, valves embedded in the conical-shaped lids failed during continuous cyclic testing and a single zone controlling the spiral heaters created a large temperature gradient within the bed. Therefore, only the TC-TSAC function (stage 2) of the CRCS system was successfully validated for CO₂ compression and production at 4.16kg/day, 20psia, and greater than 99% CO₂ purity.

In FY17, the heater coils were rewired to allow for the ability to control stage 1 heaters at multiple zone. Initial results indicated that the modified heater controls did resolve the temperature gradients issue; better-regulated power input does lower power consumption during thermal regeneration. Current efforts involve installing external stage 1 valves, implementing automatic power input, and stage 1 and stage 2 sorbent characterizations. The redesigned TC-TSAC would potentially be integrated with the 4BMS-X as an upgrade to the current CO₂ sorbent bed.

B. Liquid Thermal Amines

The development of a gas/liquid contactor for capturing (and releasing) CO₂ for microgravity applications as notionally demonstrated in Figure 7²⁹. The contactor is arranged in a cross-flow configuration wherein CO₂-laden process air is sent into the contactor perpendicular to grooved-trays containing an aqueous liquid amine. The initial focus is on diglycolamine - a secondary amine with a high capacity for CO₂ and concomitant low vapor pressure (compared to more industrially common volatile liquid amines like monoethanolamine). The water/amine mixture flows through a header and into the individual v-grooves upon which the absorbent wets and spreads across the grooves providing significant surface area for gas/liquid contact and liquid adhesion in a microgravity environment.

Recent efforts have focused on modeling mass transfer within a single groove to calculate the expected CO₂ flux using Multiphysics finite element method (FEM) software. The flux rates have been used to project the necessary contactor size to support a crew of up to four persons. Drawing upon the FEM results, a process model has also been established to investigate the dynamic performance of a contactor as a function of regeneration temperature, vehicle size, and metabolic rate changes associated with sleeping, daily activity, and exercise. These initial modeling efforts indicate the concept has merit. Secondly, the results suggest the technical approach is flexible enough that it can be tailored to a variety of mission scenarios.

Testing on contactor and degasser prototypes has also been recently initiated. The prototyping and testing efforts seek to balance several factors. For the contactor, mass transfer can be maximized by increasing the gas/liquid contact area by decreasing tray spacing to stack more trays within a fixed volume. At the same time, this reduces the characteristic length scale resulting in laminar gas flow and larger mass transfer boundary layers decreasing mass transfer efficiency. This can be offset by increasing the gas flow rate to a certain degree where a practical limit is set by the velocity at which the gas begins stripping the sorbent from the grooves (in contrast to packed beds which have traditionally been limited by pressure drop).

Degasser testing has focused on evaluating the temperature at which significant CO₂ is evaporated. The optimal temperature is the minimum temperature required to support metabolic respiration (approximately 4 kg/day CO₂ removal). Any temperature in excess of this requirement results in additional heating and higher water loss rates.

While the testing has been initiated, much optimization is still needed to understand the influence of geometry and process parameters on performance. This information will enable the refinement of models and designs and will also establish performance sensitivity to process variables. Future work is still needed to understand integrated performance and to determine how to interface and package all components required for a stand-alone liquid amine CO₂ scrubbing system. For additional information, please see the work of Rogers et al²⁹.

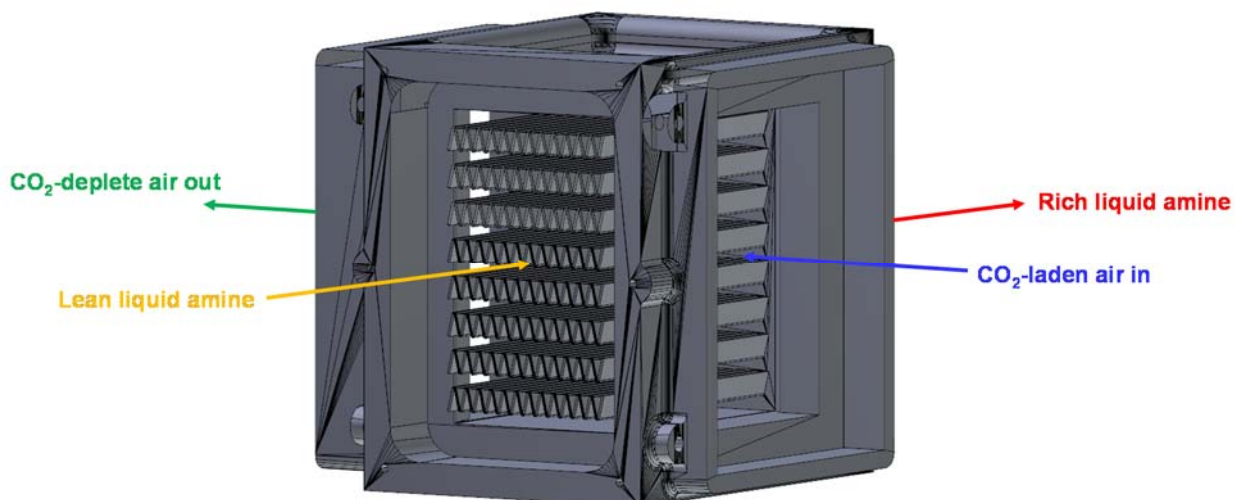


Figure 7. Notional design for a microgravity gas/liquid contactor for CO₂ capture

C. 3-D Printed Sorbent Monolith

Honeycomb monoliths loaded with metal-organic frameworks (MOFs) are highly desirable adsorption contactors because of their low pressure drop, rapid mass transfer kinetics, and high adsorption capacity. Moreover, 3D printing technology renders direct material modification a realistic and economic prospect. In this work, 3D printing was utilized to impregnate kaolin-based monolith with UTSA-16 metal formation precursor (Co) whereupon an internal growth was facilitated via a solvothermal synthesis approach³⁰.

In one approach, we fabricated two types of 3D-printed MOF monoliths from MOF-74(Ni) and UTSA-16(Co), according to a two-solution based procedure depicted in Figure 8. Briefly, the first solution was prepared by dissolving MOF powders and bentonite clay (as a binder) in ethanol. The mixture was then allowed to stir for 2 h to obtain a homogeneous solution. The second solution was obtained by dissolving Poly(vinyl) alcohol (PVA)(as a plasticizer) in DI water and ethanol and mixing for 0.5 h at room temperature followed by sonication for 30 min. In the next step, both solutions were combined and mixed using an IKA RW20 mixer at 250 rpm for 2-3 h until an extrudable paste was obtained. The paste was then loaded into a syringe (3 cc, Norson EFD, USA) and extruded from a 0.85 mm diameter nozzle (Tecchon) by pressurizing (2-5 psig) air into the syringe. Well-defined monolithic configurations with uniform channels were printed in a layer-by-layer manner.

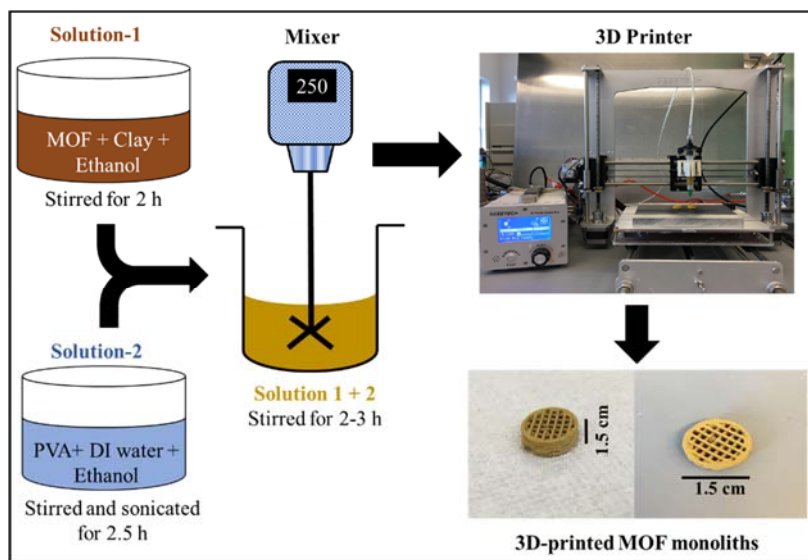


Figure 8.. Schematic of 3D-printed MOF monoliths preparation procedure

The 3D-printed MOF structures with 1.5 cm height and 1.5 cm diameter were obtained and transferred to a conventional oven for heating at 100 °C to prevent the development of cracks. The monoliths compositions are presented in Table 1.

Table 1. Compositional ratio of 3D-printed MOF monoliths

Monolith	MOF (wt %)	Bentonite Clay (wt %)	PVA (wt %)	DI Water : Ethanol (vol %)
MOF-74(Ni)	80	15	5	5 : 95
UTSA-16(Co)	85	10	5	2 : 98

The CO₂ adsorption isotherms of 3D-printed MOF monoliths and powders were measured at 25 °C, as shown in Figure 9. For additional details, please refer to the work of Lawson et al³⁰.

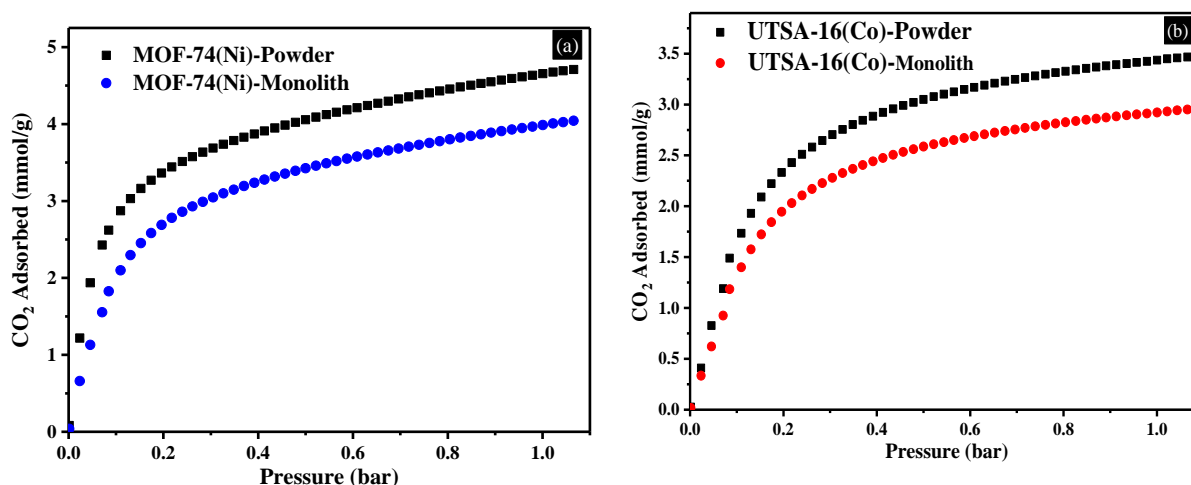


Figure 9. CO₂ adsorption isotherms of 3D-printed (a) MOF-74(Ni) and (b) UTSA-16(CO) monoliths with their corresponding powders at 25 °C and 1 bar

D. Development of Non-Dusting Binders for Traditional and Novel Adsorbents

This project is examining the application of different polymers on zeolite pellets to eliminate dusting generated during vacuum-swing adsorption cycles. The project has examined 2 different polymers and 3 different types of 13X zeolite. A polymer application method was developed that produces an even coating of polymer across the pellet as examined using SEM. The total loading of the polymers is identified by using thermal gravimetric analysis, and particle attrition is screened using a plenary ball-mill. The dusting results from the ball mill were found to be particularly sensitive to the amount of water contained in the adsorbent, and thus, a protocol was developed that provides control over the total amount of moisture in the adsorbent prior to ball mill testing. A leading candidate from ball mill screening was identified and provided to NASA for detailed attrition testing.

Initial NASA results show a reduction of dusting of approximately 30% for the polymer coated material, but adsorption data from the Glover group indicates a corresponding reduction in the CO₂ adsorption capacity of 30%. Thus far only the maximum amount of polymer coating has been examined. Specifically, polymer was added to the zeolite until it was observed to just begin coming off the zeolite surface. Optimization is currently underway to examine the tradeoff of added polymer mass and adsorption capacity to identify if a similar reduction in dusting can be obtained using a lower polymer mass. Publication of these results are anticipated in the Summer of 2019.

E. H₂O Stable MOF

In the NASA funded Phase I Small Business Innovation Research (SBIR) project (Contract No. NNX17CM55P) TDA developed a rapidly cycling vacuum-assisted thermal swing adsorption (VTSA) system that used a Metal Organic Framework (MOF) sorbent to remove CO₂ from cabin air and concentrate it for subsequent reduction and pressurization. In Phase I, TDA prepared pelletized MOF adsorbent and demonstrated its ability in selectively

removing CO₂ from the cabin air at low partial pressures (2 torr or less) and recover the CO₂ at pressure up to 150 torr (in single stage) for storage and supply to the CO₂ reduction process using a thermal regeneration (or by mild vacuum-assisted thermal regeneration). The MOF adsorbent developed is highly selective to CO₂ and very stable in the presence of main constituents of cabin air (N₂, O₂, H₂O). The sorbent adsorbs CO₂ via strong physical adsorption (the

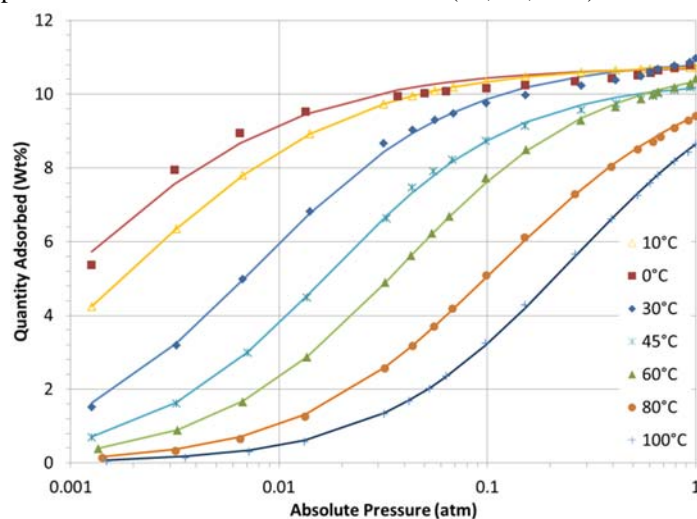


Figure 10. CO₂ adsorption isotherms on TDA's MOF adsorbent at different temperatures

at 90°C), the sorbent achieved a capacity of 2.5% wt. with a CO₂ recovery pressure of 5 torr and a capacity of 0.5% wt. at a CO₂ recovery pressure of 150 torr. For a 4-person cabin, we estimated that 6.7 kg of sorbent will meet the CO₂ removal requirement of 0.17 kg/hr, consuming 0.25 kW power and requiring 0.25 kW heat to be rejected (based on 20°C adsorption and 70°C regeneration and recovering the CO₂ at 760 torr as a pure product via a vacuum pump).

heat of adsorption is calculated as 20 kJ/mol). This relatively strong attraction enables the sorbent to achieve high adsorption capacity even when CO₂ is present at very low concentrations (it can maintain the cabin CO₂ concentration below the level at which it is currently maintained) but because no covalent bond is being formed between CO₂ and the surface adsorption sites the sorbent can be easily regenerated by changing operating conditions (i.e., applying heat or vacuum or a combination of both). Measured capacities are shown in Figure 10. In the fixed bed adsorption tests, TDA's MOD adsorbent achieved a CO₂ working capacity of up to 1.76% wt. (kg CO₂ removed per kg sorbent) under a mild temperature swing cycling the bed temperature from 20°C to 70°C where the CO₂ was recovered at around 5 torr. When increasing the temperature swing from 50°C to 82°C (adsorption at 8°C and desorption

F. Spacecraft Cabin Carbon Dioxide Capture via Deposition

The basis of this method of CO₂ capture utilizes the condensation and deposition temperature differences between N₂, O₂, and CO₂ to selectively remove CO₂ from the air stream³¹. The process involves flowing cabin air across a cold surface that is below the deposition temperature of CO₂, but above the condensation points of N₂ and O₂, and allowing the CO₂ to deposit. The CO₂-free air then re-enters the cabin. This method has the potential to be further utilized and provide humidity and trace contaminant control, as well as CO₂ storage and compression.

At a partial pressure of 2.0 mmHg, the deposition temperature of CO₂ is about 142K. If a lower partial pressure is desired, then the deposition temperature also decreases. Therefore, the operating temperature of the cold surface must be below this deposition temperature in order to overcome heat transfer effects and allow CO₂ to deposit. An additional operating parameter to consider is cabin air inlet flow rate. The higher the inlet flow rate, the more cooling power is required to deposit a sufficient amount of CO₂.

In order to test this CO₂ capture method, a Janis SC-10 Stirling cooler was procured, and the cold tip was enclosed in a chamber complete with inlet and outlet flows, pressure transducers, pressure safety valve, thermocouple feedthroughs, CO₂ meters, and a viewport, as seen in Figure 11a. At the desired deposition temperature range, the cooler has a cooling power of about 20W, which dictates a maximum flow rate of 5 slpm to capture measurable amounts of CO₂. The first test performed, in order to confirm functionality, was an input of pure CO₂ at a rate of 1 slpm. The cold tip was quickly saturated with CO₂ ice, as seen in Figure 11b, so the cooler was turned off and flow stopped. The resulting temperature profile showed 4 unique phases: cool down, deposit, sublime, and warm up. During the cool down phase, the cold tip decreased in temperature, but no CO₂ deposited. Once the cold tip reached 196K, the rate of temperature decrease slowed, as CO₂ was depositing. After shutdown, the cold tip began to warm until it reached 196K, after which the temperature did not increase until all CO₂ had sublimed. Finally, the cold tip approached room temperature. This temperature trend changed slightly for the subsequent trial runs, as the cooler was allowed to reach a steady state temperature with no gas flow first. Once gas flow was started, the temperature spiked and reached a new steady state during the deposition phase.

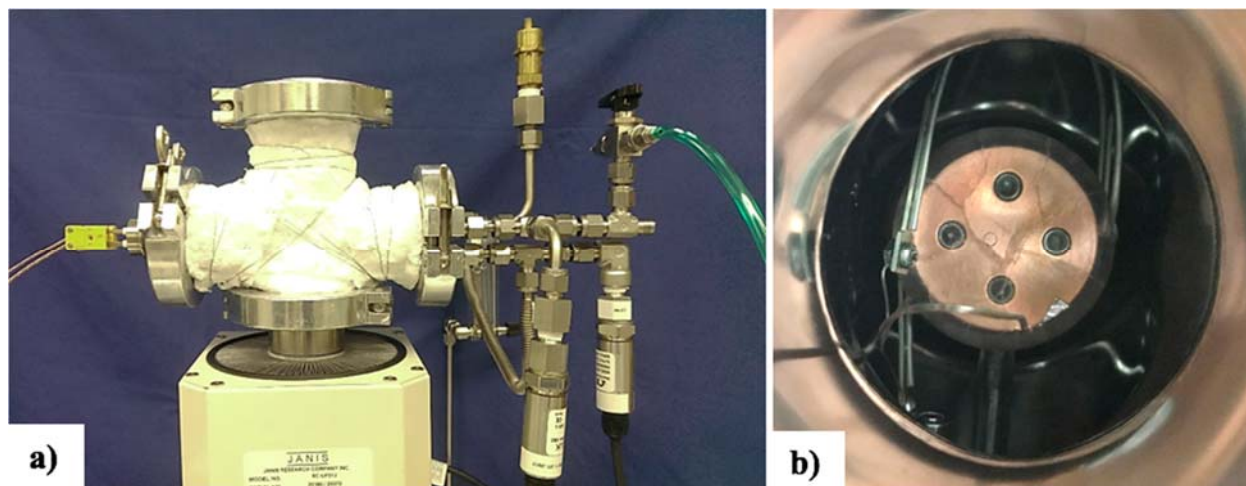


Figure 11. Janis SC-10 Stirling Cooler: a) side view of attached chamber with inlet/outlet ports and instrumentation; b) top view through viewport showing CO₂ ice on cold tip

A total of 27 trial runs were performed, following a test matrix of varied flow rate, CO₂ inlet concentration, and cooler power in order to characterize CO₂ capture efficiency. Flow rates of 1, 2.5, and 5 slpm were tested, CO₂ concentrations of 500, 2600, and 5000ppm, and cooler power of 50%-100%. All of the runs followed a general trend: as the cooler power was increased, i.e., as the cold tip temperature decreased, the percent of CO₂ captured increased to a point, then approached a maximum efficiency asymptotically. Interestingly, each flow rate and inlet concentration begin the asymptotic behavior at approximately 125K. In addition, the lower the flow rate, the higher the percent captured was.

The chosen test case of 2.5 slpm, 2600ppm, and 80% cooler power was repeated twice to both measure precision and test extended cycle CO₂ capture performance. Repeatability was excellent, with only 0.1% difference in percent CO₂ captured between each run. However, as the deposition phase was extended, the percent CO₂ captured decreased. This was shown by a logarithmic trend of the outlet CO₂ concentration vs. time.

In general, as an initial proof of concept, this simple CO₂ deposition system performed better than expected. The Stirling cooler was able to capture trace amounts of CO₂ at warmer cold tip temperatures than predicted and reached a percent CO₂ captured of over 80% without any system optimization. The performance data leads to favorable expectations for the sub-scale, cycling test system currently being constructed at ARC. For more detail on this work, please refer to the work of Belancik et al³¹.

G. Other Non-NASA Funded Technology Development Efforts

The “Other Non-NASA Technology Developments (NETL, NAVSEA/PNNL, HWI, etc.)” covers efforts that are related to spacecraft CO₂ removal, though not funded by NASA. For example, at the sorbent material development level, the National Energy Technology Laboratory (NETL) and NASA are renewing a Space Act Agreement (SAA). Through this SAA, NASA will evaluate the potential spacecraft application of solid amines produced by NETL for carbon capture applications³⁹. NASA also has a similar, though informal, agreement with the U.S. Naval Sea Systems Command (NAVSEA) to evaluate a sorbent developed by Pacific Northwest National Laboratory (PNNL)⁴⁰ for spacecraft applications. At the system level, Honeywell Aerospace Advanced Technology is developing an ionic liquid technology as described below.

1. Carbon Dioxide Removal by Ionic Liquid Sorbent (CDRILS) System Development

Unlike past and current spacecraft CO₂ removal systems, which use solid sorbents, Honeywell’s Carbon Dioxide Removal by Ionic Liquid Sorbent (CDRILS) system uses ionic liquid as the CO₂ absorbent. Ionic liquids are salts which are liquid at room temperature, and thus have a negligible vapor pressure, eliminating odors and reducing the likelihood of contaminating the purified air and downstream systems. Unlike amines, ionic liquids have high oxidative stabilities, and are generally nontoxic. The CDRILS system architecture is based on the continuous liquid sorbent system designed for submarines in the 1950s. The submarine system supports over 100 crewmembers at a time and uses relatively low volume, weight, power and cooling. This submarine system is so reliable and long-lasting that it is still used today. The CDRILS architecture is shown in Figure 12, where the ionic liquid is recirculated between a scrubber, in which CO₂ is absorbed from the cabin air, and a stripper, in which the CO₂ is desorbed and the ionic

liquid is regenerated using heat and vacuum. In the scrubber and stripper, the ionic liquid is contained and flowed within thousands of tiny hollow fibers. The fiber walls, which are air-permeable and hydrophobic, simultaneously provide air-liquid contact and containment of the liquid independent of gravity. The combination of the high surface area of the hollow fiber membrane contactors and the flow of absorbent within those fibers provides rapid CO₂ transfer between phases and allows for more CO₂ to be captured in a smaller system. Honeywell will fly a prototype of the CDRILS system on ISS in 2020 through the Center for the Advancement of Science In Space (CASIS). For further details on the CDRILS system refer to the work of Yates et al³².

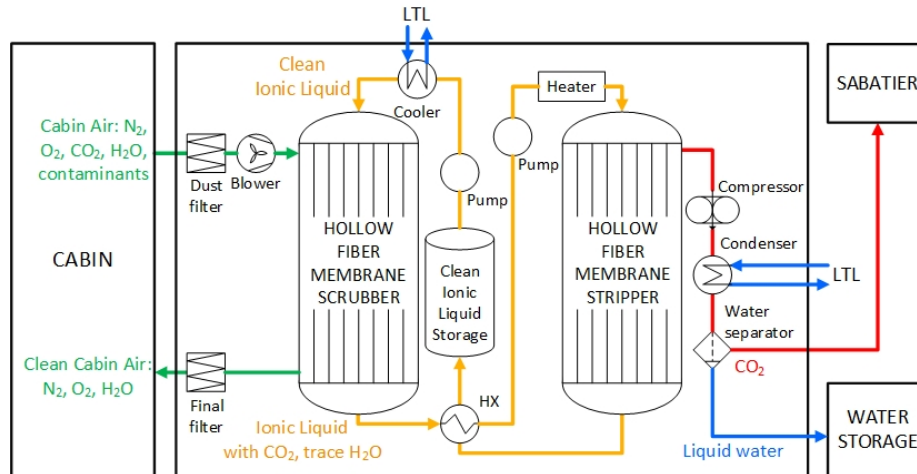


Figure 12. CDRILS Architecture

IX. Summary

In this summary paper, we have described four ISS technology demonstration development efforts, which will have the dual purpose of testing new CO₂ Removal technology candidates in a spacecraft environment and supporting a higher number of crew members on board the ISS. Six specific NASA-funded development efforts with variety of NASA funding mechanisms (AES, EPSCoR, and SBIR) were reviewed. Finally, a brief review of the ongoing work in CO₂ removal by non-NASA entities highlights the coordination between NASA and other government and commercial entities in this area.

X. Conclusions

In total, the CO₂ Removal technology development efforts suitable for Mars class missions as described in this paper may be characterized as a broad and robust effort. The on-orbit technology demonstrations should provide a high degree of confidence in the leading CO₂ removal technology candidates. The material development efforts described have the potential to augment these leading candidates with improved sorbents, or be applied to surface systems in future applications. As the other system development efforts mature and show promise, they will also be considered for flight applications through other emerging opportunities.

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