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Development of Carbon Dioxide Removal Systems for NASA's Deep Space Human Exploration Missions 2016-2017

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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

AES = Advanced Exploration Systems
AC-TSAC = Air Cooled Temperature Swing Adsorption Compressor
ARC = Ames Research Center
CDRA = Carbon Dioxide Removal Assembly
CRCS = Carbon Dioxide Removal Compression and Storage
CO_2 = Carbon Dioxide
ECLSS = Environmental Control and Life Support System
EPSCoR = Experimental Program to Stimulate Competitive Research
ISS = International Space Station
LSS = Life Support Systems
NETL = National Energy Technology Laboratory
MSFC = Marshall Space Flight Center
NASA = National Aeronautics and Space Administration
NRA = NASA Research Announcement
PSA = Pressure Swing Adsorption
SBIR = Small Business Innovative Research
SMT = Systems Maturation Team
TC-TSAC = Thermally Coupled Temperature Swing Adsorption Compressor
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, "*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-*

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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 CO_2 Removal technologies (part of a life support system) for Exploration missions are described. In general, the goal of these efforts is to develop an 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 missions. In addition, NASA-funded work underway on sorbents and systems at lower technology readiness levels (TRL) are discussed. The sorbent development efforts have the potential to be applied as upgrades to existing systems, as merited. The recent announcement of a new thrust area in the ISS Utilization NASA Research Announcement[2] (NRA) provides a new opportunity for evolving systems to be considered for development into ISS flight demonstrations.

The objective of this paper is to outline the current NASA-funded efforts in CO_2 removal systems and material development in the context of the NASA CO_2 Removal Roadmap. References are also 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 CO_2 removal technology has reliability and capability gaps that must be solved both for ISS and future Exploration missions. From FY12 to FY14, the Atmosphere Revitalization Recovery and Environmental Monitoring (ARREM) project under the Advanced Exploration Systems (AES) program included efforts to improve the CO_2 Removal state-of-the-art by seeking more robust sorbents and evaluating alternate sorbent formats and fixed-bed configurations[3-5]. 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 CO_2 removal. This recommendation was to include goals for both ISS and future Exploration missions.

As reported on in a previous paper[6], technical interchange meetings (TIMs) were held in the spring of 2014 to determine criteria and goals for Exploration CO_2 removal systems and gather information on the state-of-the-art of CO_2 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 primary 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.

NASA CO_2 removal technology development has continued under the AES Life Support System Program (LSSP) and the ISS Exploration office from FY15 to FY17[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 CO_2 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 CO_2 for the purpose of downstream processing. An example of downstream processing is the Sabatier reactor used on ISS to reduce CO_2 in the presence of H_2 (a byproduct of electrolysis used in O_2 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 on non-existent resupply opportunities, such as the Mars transport class of missions.

The CO_2 Removal Roadmap consists of three primary sections. The uppermost blue band describes current and planned on-orbit operations of experiments and technology demonstrations with relevance to exploration CO_2 removal systems. The largest section is in the center of the roadmap, and contains the milestones, decision points, and activities underway and planned in the area of closed-loop CO_2 removal. The green band near the bottom of the roadmap provides a reference for the activities relevant to the current ISS CO_2 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 (FOM) for Mars-class missions.

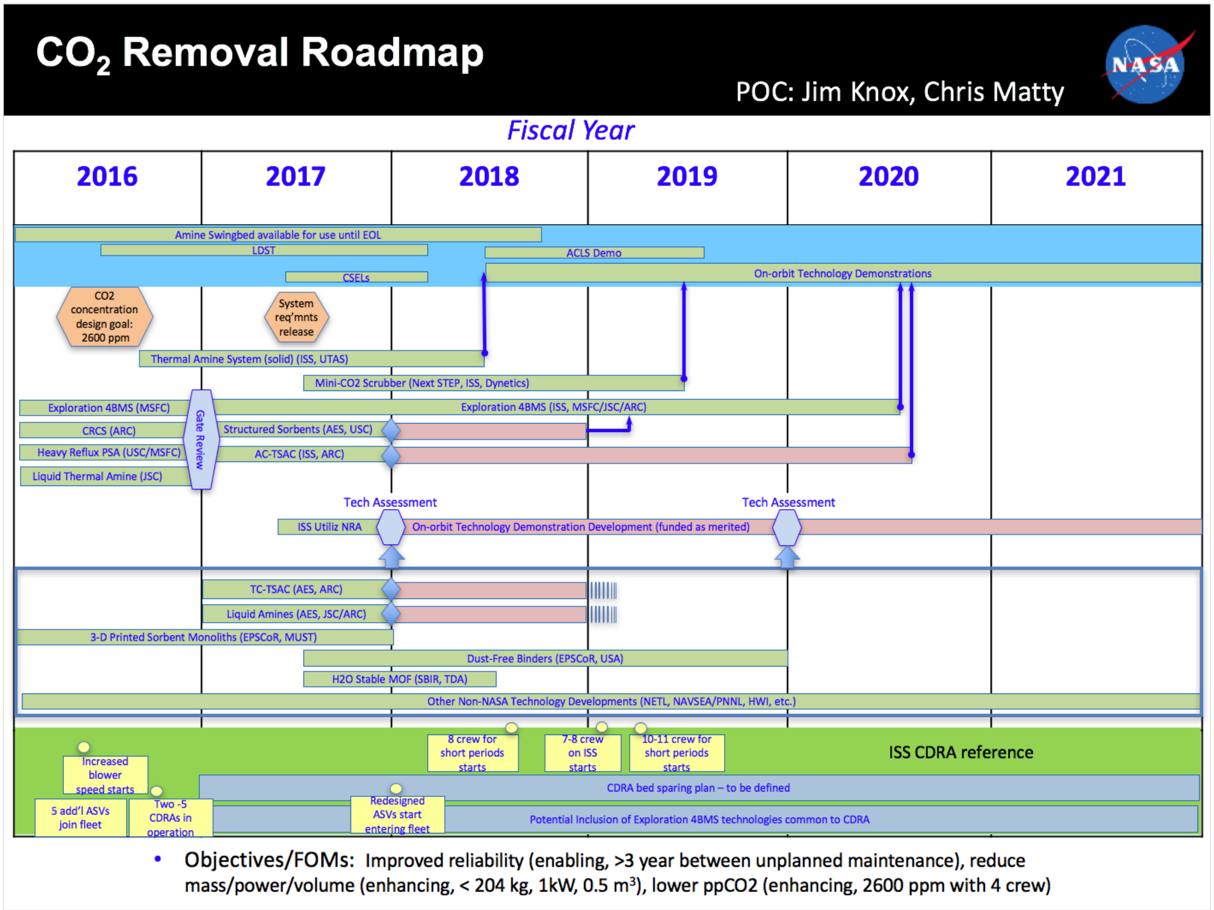
V. On-Orbit Operations

The top-most blue band in the roadmap shows current and planned CO_2 removal activities on the ISS. Each of the activities are discussed below.

A. On-orbit Technology Demonstrations

The primary near-term goal of the NASA CO_2 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 as a spacecraft must be a tightly sealed system. Thus, successful testing of potential Mars-class mission systems on the ISS provides a high degree of confidence of success for an actual Mars mission, when no opportunity exists for either emergency resupply or a rapid return to Earth.

As shown in Figure 1, the on-orbit technology demonstrations for potential NASA Mars-class mission CO_2 removal technologies are planned to begin in the middle of fiscal year (FY) 2018. 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.



CO_2 Removal Roadmap

POC: Jim Knox, Chris Matty

- **Objectives/FOMs:** Improved reliability (enabling, >3 year between unplanned maintenance), reduce mass/power/volume (enhancing, < 204 kg, 1kW, 0.5 m^3), lower ppCO2 (enhancing, 2600 ppm with 4 crew)

Figure 1. Carbon Dioxide Removal Roadmap

B. Amine Swingbed

The Amine Swingbed is an open-loop CO_2 removal technology[8] currently on-orbit that operates in a pressure swing absorption (PSA) cycle. CO_2 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 System. The Amine Swingbed has already achieved its experimental objectives of 1000 hours of operation. It has been used to augment the primary CO_2 removal systems, the U.S. CDRA[9] 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 CO_2 removal systems.

C. Long Duration Sorbent Testbed (LDST)

The Long Duration Sorbent Testbed[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 (ISS) Carbon Dioxide Removal Assembly (CDRA). 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 further inside 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.

D. Advanced Closed-Loop System (ACLS) Demo

The Advanced Closed-Loop System[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 CO_2 removal, oxygen generation and CO_2 reprocessing. After many years of predevelopment, the ACLS project started into flight development in 2011, and is currently scheduled to be deployed on the ISS in mid-2018. ACLS will be qualified as non-mission critical system hardware.

E. Capillary Structures for Exploration Life Support (CSELs)

The CSELs flight experiment[12] is intended 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 has 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 in two ECLSS areas: CO_2 removal and water recovery. 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 CO_2 Removal Roadmap. The importance of one specific requirement, cabin CO_2 partial pressure, is such that it required a dedicated forum in FY16[13-15]. 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 CO_2 partial pressure and microgravity on human physiology. In FY17, the overall CO_2 removal requirements were refined in preparation for an end-of-FY17 technology assessment[16]. These requirements had been initially defined for the FY16 Gate Review, which is discussed below.

VII. Early Flight Technology Demonstrations

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 CO_2 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 CO_2 removal capability for these crew increases two early flight technology demonstration projects (Thermal Amine System and Mini-CO2 Scrubber) have been initiated by the ISS program. These projects will also provide operational experience to help assess applicability of these technologies for exploration missions. As of this writing, negotiations on both projects were in progress. More details will become available when the contracts are in place.

VIII. FY16 Gate Review and FY17 Tasks

In late FY16, a gate review was conducted to assess the appropriate FY17 funding levels for NASA-funded CO_2 removal technology development efforts. The resource requirements (principally mass, power, and volume) were estimated by the technology developers and presented to a review board along with other supporting information on technology development status and forward plans. The review board provided a recommendation on FY17 funding for each technology. Of the four technologies assessed, three were recommended for continued funding. These are described in more detail below. Due in a large part to the substantial mass required for the vacuum pumps, the Heavy Reflux Pressure Swing Adsorption (PSA) system was not recommended for continued funding in FY17. It is worth noting that this technology may be beneficial for terrestrial low CO_2 partial pressure applications, such as chemical processing.

A. Exploration 4-Bed Molecular Sieve (4BMS-X)

The 4BMS-X was recommended for continued funding by the gate review committee, though it was suggested that reliability be further emphasized. In response, the goals of the development were revisited, and the focus shifted to selection of sorbents with higher structural stability performance over those with higher performance characteristics such as capacity and kinetics. As detailed in Ref. 7, the 4BMS-X effort includes full-scale system development and testing, structural testing of candidate sorbents, computer modeling and simulation, sub-scale testing to understand various aspects of fixed-bed sorbent physics, and sorbent characterization to provide input for the computer simulations. Recent advances in these areas are further discussed below.

1. Full-Scale System Development and Testing

Three test series have been executed with brass-board 4BMS-X system, as described in detail by Peters[17] as of this writing. The first test series confirmed that the performance for this system was consistent with performance for the flight CDRA acceptance tests[9], shown in Figure 2 as the Protoflight results. For all tests shown, the inlet conditions and operational parameters were matched as closely as possible to the Protoflight tests. The 4BMS-X results were obtained after relocation of the Performance and Operational Issues Testbed (POIST) development system[18] to a different location with a newly upgraded facility for inlet air conditioning, data acquisition, and control. This test series confirms that the changes in hardware made to the POIST system (now called the 4BMS-X system) did not affect the system performance, and validates the newly upgraded 4BMS-X test stand. The POIST 2013 test data was obtained with the POIST system located in the Environmental Control Chamber[19] (E-Chamber). Finally, the CDRA-4 Engineering Unit (CDRA-4EU) data was obtained with a system that more closely simulates the flight CDRA, particularly in the flight-like sorbent bed canisters, blower, and air-save pump[20]. CDRA-4EU testing was also conducted in the E-Chamber.

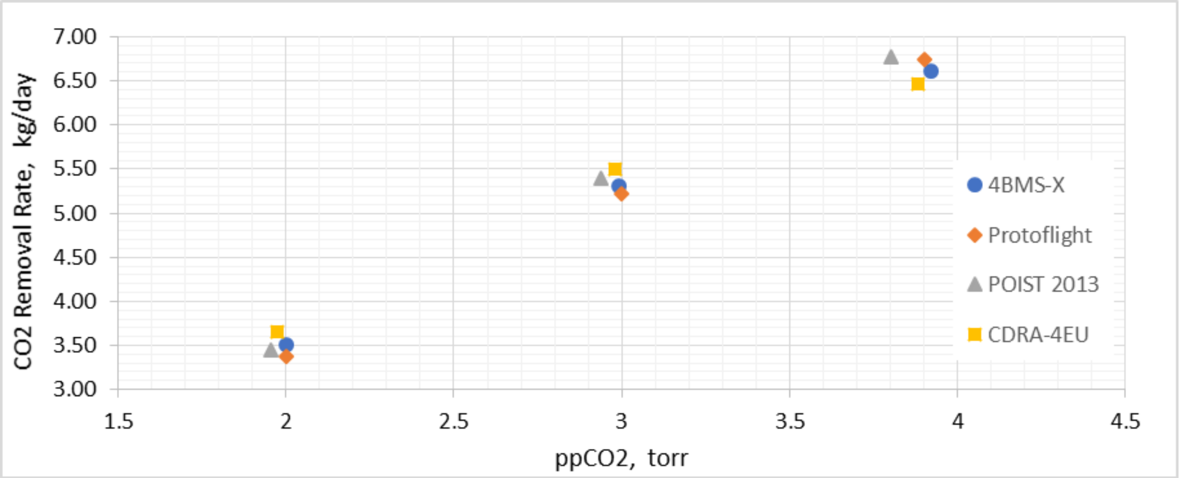


Figure 2. 4BMS-X Removal Rate vs. Inlet $ppCO_2$ in Comparison with Heritage Performance[17]

The second test series included a change in the sorbent layer scheme of the desiccant bed. The desiccant bed contains a bulk water adsorber, silica gel, and a residual water adsorber, zeolite 13X. Although the 13X serves to maintain desiccant outlet dewpoints below -90C, it also adsorbs CO_2 under normal operating conditions. This is a parasitic effect due to the CO_2 holdup in the desiccant bed, which is returned to the cabin instead of being removed. Results from this test series, as shown in Table 1, show that a performance increase of over 0.5 kg/day was achieved due to a reduction in the desiccant bed 13X quantity. The "-50% 13X" row in the table indicates that half of the original 13X quantity was removed for this test. These results also indicate that performance may be further improved by further reductions in desiccant bed 13X, especially if the desiccant bed is oversized (as indicated in the next section). An alternate approach to further 13X removal is to replace the 13X with a zeolite that has lower CO_2 capacity, such as 4A, or one that has insignificant CO_2 capacity, such as 3A. These options are being explored with a combination of computer simulations and experimental investigations.

Table 1. Increase in CO2 Removal After 50% Reduction of 13X from Desiccant Bed[17]

Test	Half Cycle [min]	$ppCO_2$ [torr]	Air Flow [SLPM]	Inlet Temp [C]	Inlet DP [C]	HX Exit Air Temp [C]	CO_2 Removal [kg/day]
Reference	10-60-10	2.02	784	11.7	10.0	17.2	4.48
-50% 13X	10-60-10	2.01	783	11.7	12.1	14.4	5.04

Another significant finding from the 4BMS-X testing was the strong indication that the desiccant bed is oversized for nominal operating conditions. Even after the removal of 50% of the 13X in the desiccant bed, the outlet dewpoint remained below -90C despite being challenged with a high flow rate (778 slpm, or 27.5 scfm), long cycle times (360 vs. 160 minutes) and inlet humidity at the high end of the typical operating range (10C or 50F dewpoint). Following a lengthy run at these conditions, no evidence of water breakthrough was observed. To capture the desiccant bed water capacity for nominal conditions, it was determined that a breakthrough test (constant inlet feed without cycling) was required. The results of this test, shown in Figure 3, show that the water did not breakthrough the desiccant bed for over four hours of operation, or nearly twice the nominal adsorption period, indicating that the desiccant bed is oversized for these operational conditions.

The 4BMS-X system outlet CO_2 partial pressure is also shown in Figure 3. Initially we observe the expected CO_2 spike at the beginning of a cycle due to the CO_2 in the desorbing desiccant bed traveling to the system outlet. Following the CO_2 spike, the outlet CO_2 remains nearly zero until about 2 hours into the test, when beds become saturated at the inlet CO_2 partial pressure and CO2 breakthrough occurs. Interestingly, the CO_2 outlet partial pressure exhibits the roll-up phenomenon starting at about four hours. Here the CO_2 previously adsorbed onto the zeolite begins to be displaced by the water front, which has now traveled out of the desiccant bed and into the CO_2 sorbent bed.

The results from this test indicated that a further desiccant bed size reduction is a viable option to reduce the parasitic capture of CO_2 in the desiccant bed 13X layer. The excess capacity demonstrated here also allows for consideration of a residual desiccant with lower capacity and slower kinetics, but also lower CO2 capacity such as zeolite 3A or 4A.

For a complete description of the 4BMS-X and the tests summarized above, please refer to the work of Peters and Knox[17].

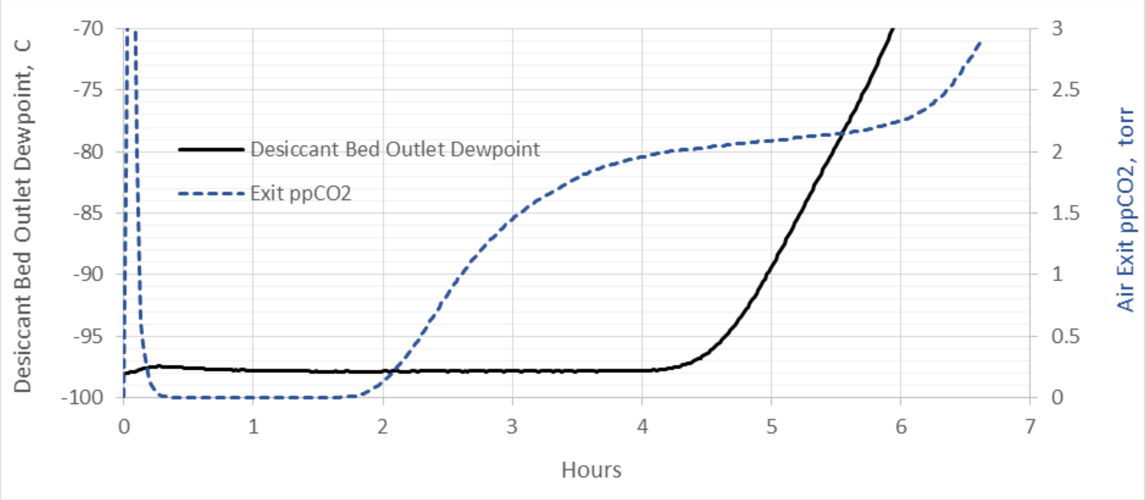


Figure 3. Desiccant Bed Breakthrough Test Results[17]

2. *Sorbent Screening and Characterization*

Recent sorbent screening and characterization results are provided in the work by Cmarik et al.[21]. Prior work in this area is discussed in References 3 to 6 and 21. The structural characterization work may be summarized by the charts shown in Figure 4, showing (a) pellet crush test results, (b) bulk crush test results, (c) attrition test results and (d) hydrothermal stability test results. Note that, while high strength in the pellet and bulk crush tests is desirable, lower values in the attrition and hydrothermal stability tests are preferred. These tests show that although no single sorbent has superior performance in all structural areas, the chosen sorbent for CO_2 adsorption, Grade 544 13X, ranks at or among the highest in bulk crush, attrition, and hydrothermal stability results.

Other important factors in the selection of a CO_2 sorbent are the equilibrium capacity and kinetics. The first factor determines the ultimate capacity and the second how quickly the equilibrium capacity is obtained. The works of Cmarik[21] also includes equilibrium capacity isotherms compiled from studies at both MSFC and ARC[22]. Grade 544 13X is shown to have superior capacity and kinetics compared with the current sorbent used in CDRA, and thus may allow for smaller fixed beds than the current system.

Other ongoing work described by Cmarik et al. is the investigation of alternate desiccants for residual water vapor removal to reduce or eliminate the parasitic CO_2 holdup in the desiccant bed.

The final aspect, discussed in detail by Cmarik, is the ability for a CO_2 sorbent to fully regenerate from an off-nominal event where humidity is allowed to adsorb on the sorbent, which has a strongly negative effect on the CO_2 adsorption capacity of zeolites. Thermogravimetric Analyzer (TGA) testing showed that the selected sorbent, Grace Davison Grade 544 13X, is able to fully recover from such an event at the 4BMS-X regeneration temperature of 200C. This result was confirmed by full-scale testing as reported by Peters and Knox[17].

For a complete description of the sorbent screening and characterization tests summarized above, please refer to the work of Cmarik et al.[21].

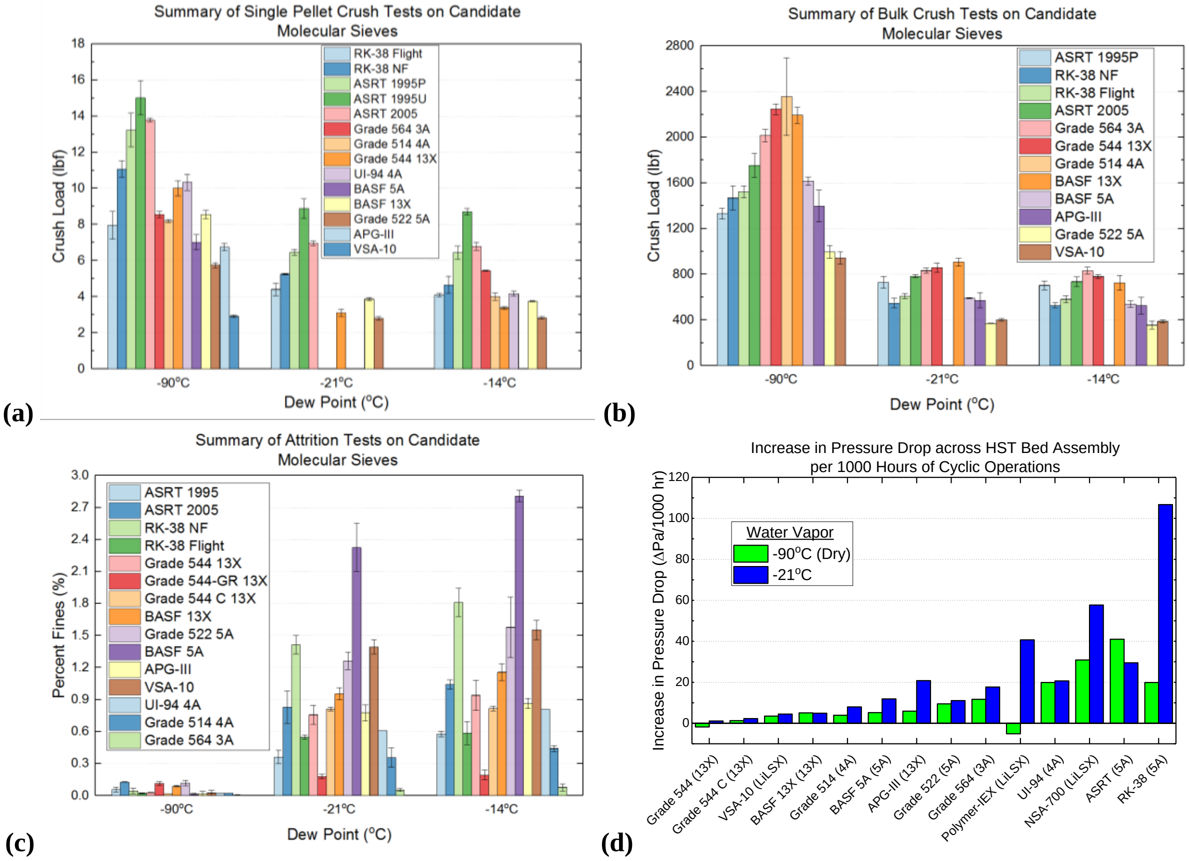


Figure 4. Structural Characterization Results: (a) Single Pellet Crush Tests, (b) Bulk Crush Test, (c) Attrition Tests, and (d) Hydrothermal Stability Tests[21]

3. Computer Modeling and Simulation

The development of a 4BMS computer simulation was documented in numerous references[6, 7, 23-26]. It is now being used for the simulation-aided design of the 4BMS-X as described in the work of Giesy et al.[27]. The preliminary results show that reductions in desiccant bed size and sorbent bed size when compared to the International Space Station configuration are feasible while still yielding a process that handles at least 4.16 kg/day CO_2. The results also show that replacement of the current CO_2 sorbent for improved structural integrity is likewise feasible.

Table 2 provides a summary of simulation results from six 4BMS-X configurations, including the CO_2 sorbent, the process flow rate, the sorbent bed size as a percentage of the ISS CDRA sorbent bed size, the calculated CO_2 removal rate and the CO_2 efficiency. For each of the six studies, the residual desiccant amount was reduced to 45% of the ISS CDRA value. Furthermore, four different CO_2 sorbents were studied as candidates for the CO_2 sorbent from the ISS CDRA. In each configuration, the sorbent bed size was decreased when compared with the CDRA sorbent beds, with the amount of the decrease depending on the sorbent.

For a complete description of the 4BMS-X computer modeling and simulation work described above, please refer to the work of Giesy et al.[27].

Table 2. A Summary of the Simulation Results from the Six 4BMS-X Configurations Considered in the Work of Giesy et al.[27]

CO_2 Sorbent	Flow Rate (SCFM)	% of Nominal CDRA bed	CO_2 Removal Rate (kg/day)	CO_2 Efficiency
RK-38	24.25	70	4.21	0.81
VSA-10	24.25	40	4.32	0.84
544 13X	28	60	4.50	0.76
544 13X	26.75	60	4.47	0.79
APG III	28	55	5.14	0.86
APG III	24.25	55	4.26	0.82

Simulation-aided design also plays a role in the mechanical design of the 4BMS-X CO_2 sorbent beds. A new heater design is required for the cylindrical beds used for the 4BMS-X (vs. the beds with rectangular cross-section in the ISS CDRA). In the work of Schunk et al.[28] a 2-D Thermal Desktop®[29] analysis of potential heater designs was conducted to optimize geometry for minimal heater power and radial thermal gradients. The 2-D model was also used to down-select between the three options. For the selected approach, a 3-D version of the model was used to analyze both radial and axial gradients as well as end effects.

The heater design options are shown in Figure 5. The spiral option consists of heater sheets that are conceptually similar in construction to the CDRA Kapton heater sheets, but in an Archimedes spiral arrangement instead of parallel sheets in the CDRA heater core. The star option utilizes cartridge heaters and star-shaped fins to distribute heat more uniformly. The structured star option is similar to the star option, but with a more regular geometry.

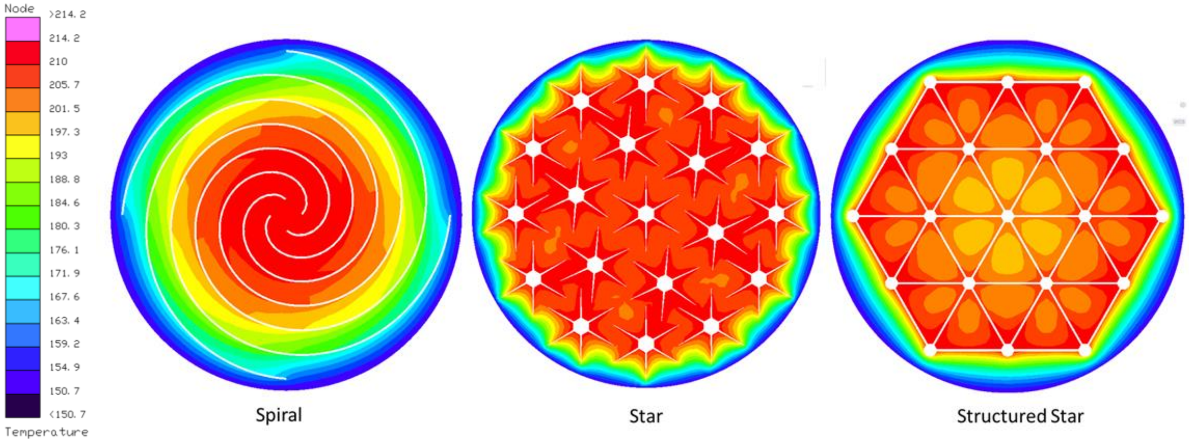
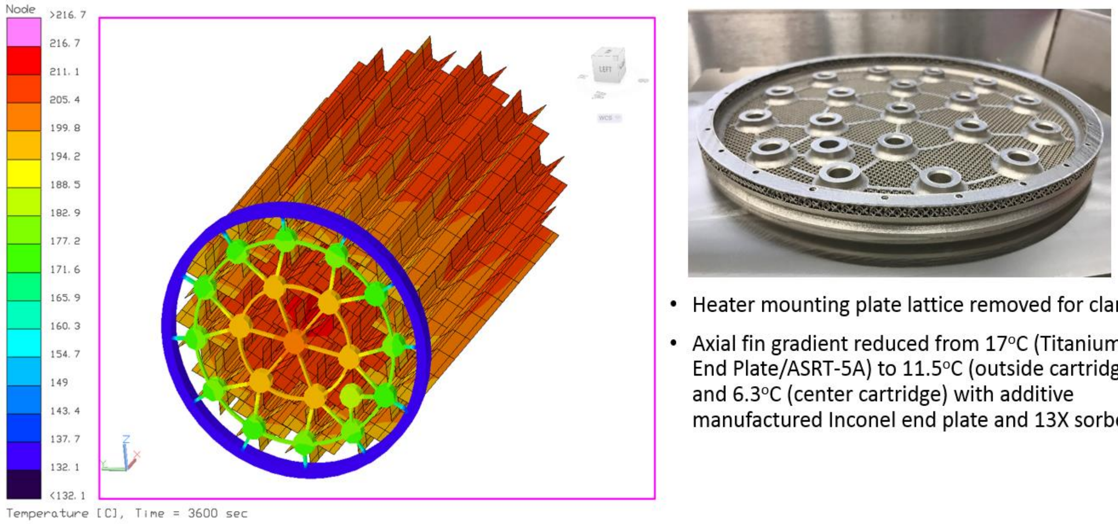


Figure 5. 4BMS-X Heater Configuration Options[28]

Temperature results from the 2D analysis are also shown in Figure 5. Here the temperature distribution for the star option is clearly more uniform. Another factor leading to the selection of the star option are its high temperature tolerance compared to the spiral sheet heater option. Anomalies with the ISS CDRA sheet heaters[30] have been associated with operating temperatures near the temperature limit of materials used in its construction. A final reason for selection of the star option is that flow channeling, which negatively affects process efficiency, is least encouraged by this arrangement. The star option was further considered via a 3D analysis of the CO_2 sorbent bed.

Initial 3D analysis results revealed a large temperature gradient in the axial direction due to heat leaks through the heater mounting plate into the external canister. Guided by results from the 3D model a series of changes were made to the bed geometry. These included limiting the contact area between the mounting plate and canister, and making use of additive manufacturing to greatly reduce the conductance of the heater mounting plate. As a result of these changes, the axial gradient was greatly reduced. The simulation results and additive manufacturing heater mounting plate may be seen in Figure 6.

For a complete description of the 4BMS-X CO_2 sorbent bed heater computer modeling and simulation work described above, please refer to the work of Schunk et al.[28].



- Heater mounting plate lattice removed for clarity.
- Axial fin gradient reduced from 17°C (Titanium End Plate/ASRT-5A) to 11.5°C (outside cartridge) and 6.3°C (center cartridge) with additive manufactured Inconel end plate and 13X sorbent.

Figure 6. 4BMS-X CO_2 Sorbent Bed Heater 3D Model Results and Additive Manufacturing Heater Mounting Plate[28]

B. Structured Sorbents

Structured sorbents are under consideration for use in the 4BMS-X, as they have the potential to eliminate dust production observed with pelletized zeolites and the associated equipment problems. However, to make this possible under the 4BMS-X flight demonstration timeline the structured sorbent design must allow for direct replacement of the pelletized zeolite in the 4BMS-X CO_2 sorbent bed. A recent evaluation of structured sorbents is provided in the work of Ritter[31] where four structured sorbent types used in temperature/vacuum swing adsorption (TVSA) processes are evaluated: rotary honeycomb wheels, electric (or potential) swing adsorption monoliths, hollow fiber contactor sorption membranes, and thermally conductive monoliths made of carbon or metal (e.g., Catacel's parallel channel metal foil structures). In TVSA processes, the sorbent is regenerated via an increase in temperature and decrease in total pressure. The advantages and disadvantages of each structured sorbent type is discussed briefly below.

- Rotary Honeycomb Wheels have the advantages of high throughput and simplicity. However, for vacuum-assisted operation in the CO_2 sorbent beds, the present seals would require redesign.
- Electric Swing Adsorption Monoliths apply electricity directly to the monolith, which provides good heat distribution, and have effective sorbent densities similar to pelletized systems. The primary drawback is the inherently slow cooling times associated with the electrically conductive material.
- Hollow Fiber Contactor Sorption Membranes are an interesting hybrid application combining zeolites and membranes. The slow cooling times are overcome by flowing a thermal fluid through the

membrane, while zeolite resides in the shell side, imbedded in the wall of the hollow fiber. Effective zeolite density is calculated to be 50% that of traditional fixed beds. The negative aspects are the complications of the fluid cooling loop and single point failure due to the loss of any single fiber.

- Thermally Conductive Monoliths represent a simple approach to rapid cooling via a metallic film coated with zeolite. Coating thicknesses are optimized for rapid mass transfer. Cooling is most effective with a cooling fluid but may also be achieved with the process air stream. Currently, however, the effective bed density is only about a third of that in a fixed bed, necessitating faster cycle times or an increase in coating thickness.

Clearly, each of the structured sorbent options have advantages and disadvantages for this application. Other factors discussed in Ritter's work include technical maturity, availability of appropriate sorbents, and impact to the overall 4BMS-X design. Based on all these factors, the thermally conductive monoliths were selected for continued investigation through computer modeling and simulation, and testing of a prototypic monolith provided by Catacel$_{JM}$ as shown in Figure 7. Internal heating via a cartridge heater at the monolith centerline will also be investigated. The practicality of both increasing coating thickness and reducing cycle time will be explored as part of this work.

For a complete description of the Structured Sorbent efforts described above, please refer to the work of Ritter[31].

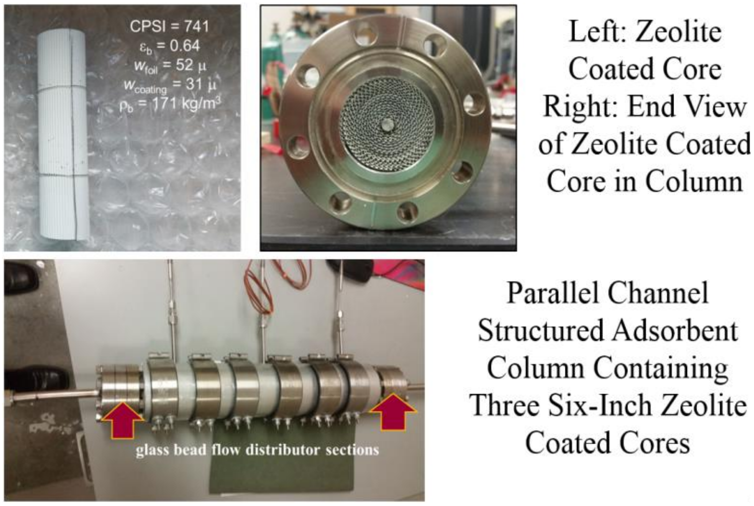


Figure 7. Parallel Channel Structured Sorbent in Test Apparatus

C. Air-Cooled Temperature Swing Adsorption Compressor

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 Sabatier 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 Temperature Swing Adsorption Compressor (TC-TSAC).

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, the AC-TSAC is being developed in parallel with the 4BMS-X. 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 system 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 CO_2 to a downstream CO_2 reduction system. This technology has been previously tested in

Figure 8. AC-TSAC Undergoing Preparation for the Integrated Atmosphere Revitalization Tests[34]

an integrated configuration with a development 4BMS system as shown in Figure 8[32-34]. Current efforts include a more complete trade study vs. a mechanical compressor and accumulator, and the selection of a replacement material for the obsolete sorbent. For more details on this system please refer to references 32 to 34.

IX. ISS Utilization NRA and FY17 Technology Assessment

The NASA Research Announcement (NRA) soliciting Research Opportunities for International Space Station Utilization[2] was originally released on November 14, 2012, with the following scope:

"This announcement is for the development of experiment hardware with enhanced capabilities; modification of existing hardware to enable increased efficiencies (crew time, power, etc.); development of tools that allow analyses of samples and specimens on orbit; enhanced ISS infrastructure capabilities (ex. Communications or data processing); and specific technology demonstration projects as detailed below".

On April 24, 2017 a new thrust area, CO2 Removal Technologies, was added to the NRA with the following description:

"Revitalization of a human-rated spacecraft's atmosphere is a critical function of the vehicle's life support system and removal of crew metabolic carbon dioxide (CO_2) comprises a significant portion of this function. NASA is pursuing alternate CO_2 removal technologies for future spacecraft that may prove more reliable than the current system aboard the International Space Station (ISS).

NASA intends to perform a technology assessment review in late 2017 to rank candidate CO_2 removal systems. The results of this activity will provide critical information toward selecting a system or systems to be further developed for potential flight demonstration aboard the ISS. The purpose of the flight demonstration is to gain extended in-flight operation experience using ISS as a proving ground for future long-duration missions."

This NRA provides the developers of CO_2 Removal systems the opportunity to submit proposals to the FY17 technology assessment and compete in the selection of an ISS flight demonstration. The re-occurrence of future technology assessments will depend on available funding and the availability of the ISS for future flight demonstrations.

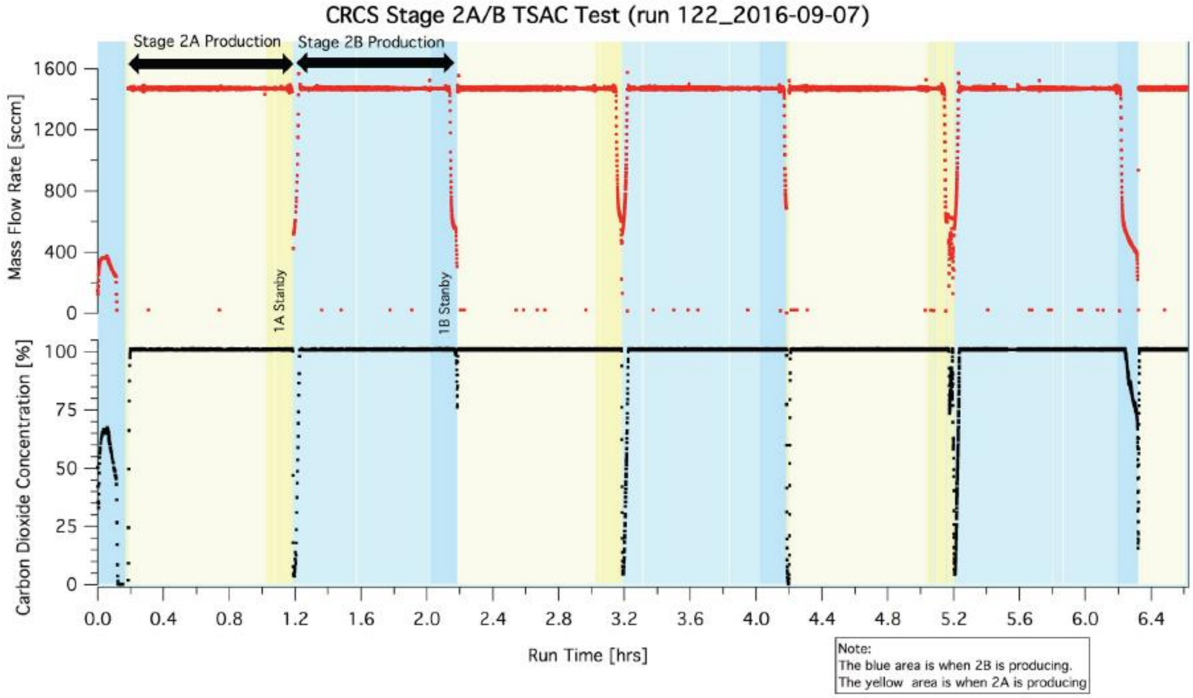
The following sections provide information on CO_2 Removal systems, system components, and sorbent materials currently under development. These CO_2 Removal systems have the potential to become flight demonstrations, while the system components and sorbent materials could be incorporated into existing or future CO_2 removal flight demonstrations.

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

Due to issues with the valve design in the Carbon Dioxide Removal and Compression System (CRCS) and the time-critical schedule for the 4BMS-X flight demonstration development, it was decided at the FY16 Gate Review to continue development of the CRCS but independently of the 4BMS-X flight demonstration.

The CRCS was renamed to the TC-TSAC[35]. This system consists of a hybrid fixed bed that contains a CO_2 removal stage (stage 1) in a conventional fixed bed, and a TSAC (stage 2) in a concentric cylinder around stage 1. Despite the stage 1 valve failure and concomitant loss of stage 1 functionality, the recent work of Richardson et al. showed that operation of the TSAC function was successful, providing nearly continuous flow of CO_2 at greater than 99% purity as shown in Figure 9. Continuing work on this system includes replacement of the damaged stage 1 valves, finding a replacement for the obsolete stage 2 sorbent, and redesigning the internal stage 1 heaters to correct for large temperature gradients observed during stage 1 thermal regeneration. The redesigned TC-TSAC would potentially be integrated with the 4BMS-X as an upgrade to the current CO_2 sorbent bed.

Please refer to the work of Richardson et al. for further details on this work.



Note:
The blue area is when 2B is producing.
The yellow area is when 2A is producing

Figure 9. TC-TSAC CO_2 Production Rate and Concentration[35]

E. Liquid Thermal Amines

Liquid thermal amines is a concept that uses liquid amines as a CO_2 sorbent in a similar fashion to the CO_2 removal systems in many submarines. However, this concept differs in two significant ways: (1) on a Mars-class mission, the system must function in microgravity for an in-transit system and in less than 1G on the Martian surface, and (2) an alternate amine must be selected that is less volatile (and thus less smelly!). The current approach is called direct liquid contact, where the cabin air flows across the liquid amine, which is in the form of a thin film and adheres to a capillary support structure. Current efforts in this development are the selection and characterization of a liquid amine and the design of the contactors and degassers for the absorption and desorption steps.

1. Liquid Amine Selection and Characterization

Based on a review of various liquid sorbents, the following criteria were selected as the most important in the selection of a liquid amine:

1) Toxicity – The sorbent must be benign enough to use in a closed environment over long periods of time without risk to crew health or experimental conditions (i.e. toxic to plant life).
2) Vapor pressure – separate from toxicity, a high vapor pressure will increase the need for sorbent replenishment and/or necessitate condensers to recover sorbent vapors
3) Odor – some sorbents have a known foul odor (monoethanolamine used on submarines reportedly caused the vessel to smell like a chicken coop). Given the psychological demands of long duration spaceflight, it would be disagreeable to utilize a sorbent that is disagreeable to the human sense of smell.
4) Capacity at 2000 ppm – As target conditions are 2000 ppm CO_2, the liquid needs to be able to absorb substantial amounts of CO_2 at this pressure.
5) Regeneration temperature – If the liquid is to be regenerated through a thermal vacuum arrangement, increasing temperature will require greater regeneration power and increase in the vapor pressure during regeneration. In order to have an energy efficient system, a low regeneration temperature is desired
6) Mass transport rate – A high mass transport rate is required in order to minimize device size.

A number of potential sorbents were tested, including several amines (primary, secondary, and tertiary), an ionic liquid, and various solvents. After conducting capacity tests, flux experiments, vapor pressure comparison, regeneration analysis, and a toxicology investigation with the JSC safety and human health directorate, diglycolamine was selected as the favorable sorbent. Ongoing tests include trace contaminant exposure, DGA life cycle testing, and an in-depth collection of thermal property and local chemistry data. Further information on current efforts to select and characterize and select liquid sorbents may be found in Rogers et al.[36].

2. Capillary Structures: Design of the Contactors and Degassers

Knowledge of liquid morphology in microgravity is limited and currently under investigation. Ref. 37 presents the study and findings of an experiment conducted on NASA's C-9 reduced gravity aircraft examining viscous liquid behavior in a capillary driven 3D printed microchannel direct air/liquid contactor through a closed loop system. The use of liquid systems in space is challenging due to controlling and balancing fluid flow, the complexity of direct air/liquid contacting, and separation of gas and liquid phases. In the absence of gravity, free floating liquids form a sphere in order to minimize surface energy in a favorable surface area to surface volume ratio. When in contact with a solid, liquids adhere to the solid surface via surface tension and form a concave meniscus at the air/liquid interface to maintain surface energy minimization. At the liquid/solid interface, capillary action can assist with flowing of the liquids in thin film configurations. The development of additive manufacturing such as 3D printing has allowed for the creation of complex capillary structures. As an assembly, these capillary structures can be linked and formed into a microchannel contactor, which allow for large surface area of air/liquid contact in microgravity and uniform fluid flow management.

A capillary contactor was flown and tested on NASA's C-9 reduced gravity aircraft[37]. The capillary contactor on the C-9 flight and a depiction of the operating theory is shown in Figure 10. The robustness of liquid thin films in microgravity and the capillary channel contactor's ability to control fluid flow during direct air/liquid contact were key areas of interest for this investigation. The experiment used a nonhazardous working fluid (vegetable oil) with similar viscosity of 40 cP to the selected liquid sorbent, diglycolamine, discussed in the liquid amine section. Achieving uniform liquid flow throughout the reactor proved to be difficult. A balancing act between the inlet and outlet needle valves had to be manually performed each parabola. When the inlet flow rate exceeded the outlet rate, the microchannel contactor would overflow, causing the annular film to thicken and protrude. When the outlet flow rate exceeded the inlet rate, a fully developed film around the reactor's air/liquid contacting surface did not form. When the correct pumping management was performed, the team was successfully able to deploy a thin film in direct air/liquid contact. However, maintaining equilibrium of the film was challenging. This experiment taught the team the importance of fluid management and system plumbing. Although the film alternated between protruding and cavitation, the liquid maintained contact with the contactor in microgravity because of capillary forces and did not release into the surrounding atmosphere. The Capillary Structures for Exploration Life Support (CSELs) flight experiment described earlier is expected to provide a better understanding of the fluid management mechanisms inherent to thin film capillary flow and direct liquid contact, and thus guide the contactor designs. Further information on the reduced gravity flight may be found in the work of Rogers et al. in Ref. 37.

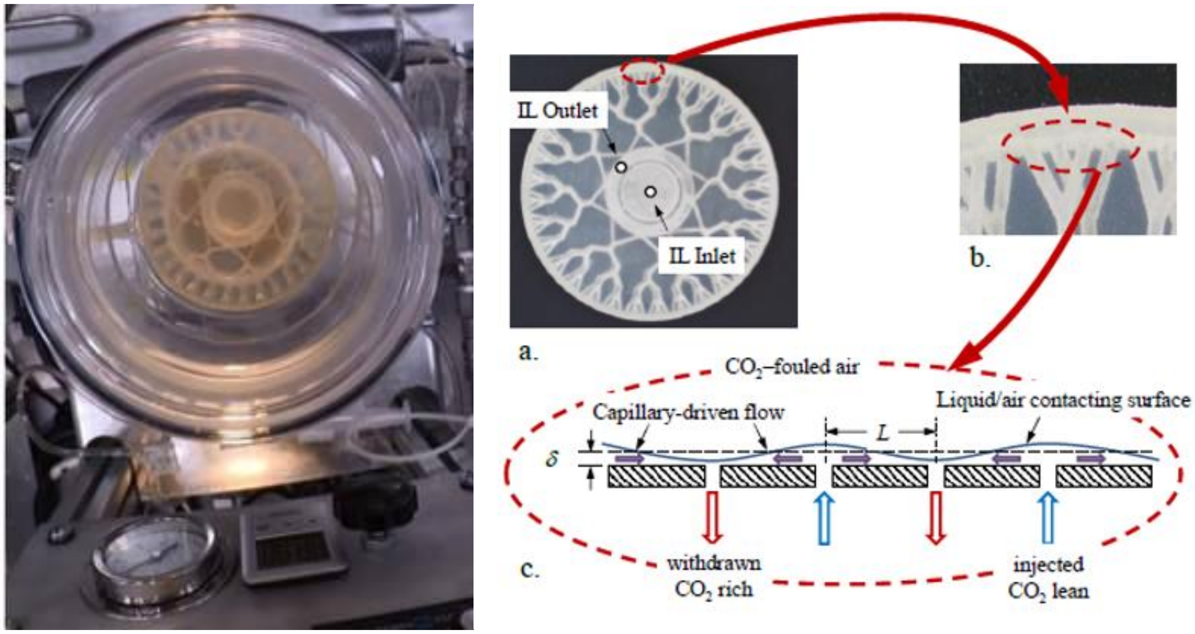


Figure 10. Capillary Microchannel Reactor in Reduced Gravity Aircraft Experiment[37]

F. 3-D Printed Sorbent Monolith

A recent development in structured sorbents is the 3-D printing of zeolite monoliths using Robocast printer[38]. As with other structured sorbents, this approach has the potential to completely eliminate the dusting resulting from attrition in a fixed bed of zeolite pellets. An advantage inherent to 3-D printing is the greater degree of control over strand size and spacing compared with honeycomb extrusions, allowing the structure to be optimized with respect to mass transfer and pressure drop for a specific application. The testing in the work of Thakker et al. showed comparable (nearly 90%) CO_2 capacity for 5A and 13X monoliths when compared with 5A and 13X powders. Favorable results for structural strength and adsorption kinetics were also obtained. Ongoing work includes the refinement of the 3-D printing methodology and incorporation of alternate sorbents.

For additional information on this project, please see the work of Thakkar et al.[38].

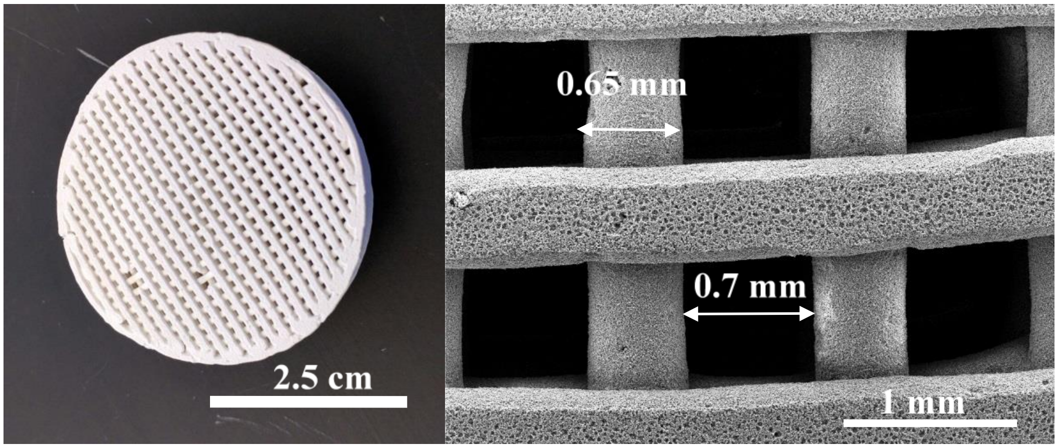


Figure 11. Prototypic Zeolite Monoliths Extruded by a 3-D Robocast Printer[38]

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

This Experimental Program to Stimulate Competitive Research (EPSCoR) effort proposes to develop binders for traditional zeolites and MOF adsorbent powders that will provide effectively zero dusting when regenerated numerous times under vacuum and heat. To eliminate dusting, adsorbent will be formed using novel binders. The effectiveness of pellet encapsulation at eliminating adsorbent dust will be quantified by measuring the pressure drop across an adsorbent bed containing the encapsulated pellets during numerous adsorption and regeneration cycles. Additionally, pellets will be formed from adsorbent powders by pressing the powders with polyvinyl alcohol or clay binders.

As this EPSCoR effort was very recently initiated, no publications are yet available.

H. Other CO_2 Removal Development Efforts

The final two green bars are briefly summarized in this section. The “H_2O Stable MOF” task refers to a Small Business Innovative Research (SBIR) award that, of this writing, was in the final stages of negotiations. Upon award, details will be provided on this effort.

The “Other Non-NASA Technology Developments (NETL, NAVSEA/PNNL, HWI, etc.)” covers efforts that are related to spacecraft CO_2 removal, though not funded by NASA. 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 applications[39]. 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. Finally, Honeywell International (HWI) is investigating ionic liquids as a safer alternative to liquid amines for spaceflight, while retaining the advantage of low regeneration temperatures[41]. This effort has been selected as an ISS flight experiment by the Center for the Advancement of Science in Space (CASIS).

X. Summary

In this summary paper, we have described four ISS technology demonstration development efforts, which will have the dual purpose of testing new CO_2 Removal technology candidates in a spacecraft environment, and supporting a higher number of crew members. The ISS Utilization NRA now includes a CO_2 Removal thrust area, providing an avenue for other technologies to be considered for development into flight demonstrations. Five specific NASA-funded development efforts were reviewed with variety of NASA funding mechanisms (AES, EPSCoR, and SBIR). Finally, a brief review of the ongoing work in CO_2 removal by non-NASA entities highlights the coordination between NASA and other government agencies in this area.

XI. Conclusions

The development of CO_2 Removal technologies 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 CO_2 removal technology candidates. The additional material development efforts described have the potential to augment these leading candidates with improved sorbents. As the other system development efforts mature and show promise, they will also be considered for flight demonstration development through the recently released CO_2 Removal Thrust area in the ISS Utilization NRA.

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