Advances in Zeolite CO_2 Removal System Design for Dust Mitigation

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Although zeolite based carbon dioxide CO_2 removal systems have historically been used successfully on Skylab and the International Space Station (ISS), there have been high-profile issues related to zeolite dusting on the ISS. As of 2014, the zeolite-based Carbon Dioxide Removal Assembly (CDRA) had the dubious honor of requiring more crew maintenance time than any other system on the ISS. In 2021, a new zeolite-based system, the Four-Bed CO2 Scrubber (FBCO2), was launched to ISS. Based on analysis of the retention filters after two years of operation, the dust production rate was reduced by over two orders of magnitude vs. CDRA. This paper reviews the filter analysis and discusses the intensive effort in the FBCO2 design process to mitigate zeolite dust production.

Acronyms and Nomenclature

2BMS	=	2-Bed Molecular Sieve
4BMS	=	4-Bed Molecular Sieve
ASV	=	Air Selector Valve
CCAA	=	Common Cabin Air Assembly
CDRA	=	Carbon Dioxide Removal Assembly
CHX	=	Condensing Heat Exchanger
CO_2	=	carbon dioxide
ECLSS	=	Environmental Control and Life Support System
FBCO2	=	Four-Bed Carbon Dioxide Scrubber
H_2O	=	water or dihydrogen oxide
HC	=	half-cycle
ISS	=	International Space Station
MSFC	=	Marshall Space Flight Center
NASA	=	National Aeronautics and Space Administration
RCRS	=	Regenerative CO_2 Removal System
RTV	=	room-temperature vulcanizing
SBAR	=	Sorbent Based Atmosphere Revitalization

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I. Background

A. Nature of Zeolites

ZEOLITES are a crystalline, high surface area mineral originally of volcanic origin. Perhaps the best known, and widespread, use of zeolites is in petroleum refining. From Degnan [1], "Zeolites, or more broadly molecular sieves, can be found in a majority of the major catalytic processes in today's petroleum refinery". Zeolites are also employed in many non-petroleum applications as illustrated by Li et al [2] in Figure 1.

For both catalysis and adsorption applications, many zeolite variations have been synthesized to achieve high capacity and selectivity for specific molecules. This has resulted in an extremely fine crystalline structure, an example of which is shown on the right side of Figure 2. Here the size of each pore is approximately 5 angstroms. Due to this extremely fine structure a teaspoon of 13X zeolite has approximately the surface area of a football field.



Figure 1. Non-Petroleum Commercial Zeolite Applications [2]

As applied to adsorption in air revitalization systems, the ionic charge of the zeolite is a major factor in the capacity for polar molecules. Both water (H_2O) and carbon dioxide (CO_2) are strongly captured in the zeolite crystal pores due to electrostatic charges. H_2O is preferably adsorbed over CO_2, which is preferred over non-polar nitrogen and oxygen molecules. The preference for H_2O over CO_2 can be strong enough, depending on the specific zeolite, to obstruct CO_2 adsorption, requiring desiccation of the air stream prior to CO_2 adsorption.

Clay is used to bind the approximately 2-micron crystals [3] into larger pellets as shown in the center and left side of Figure 2 to reduce packed bed resistance to air flow [4]. Pellet formulation is designed to favor high porosity to facilitate gas flow from the free stream into the pellets, however, this results in the pellets being friable. As a result, care must be taken in system design to prevent significant degradation of zeolite pellets into dust and resulting issues. Dusting has caused maintenance issues in some applications. This paper will review applications that have successfully mitigated dust generation and the resultant maintenance issues, as well as one application that was less than successful in these respects.

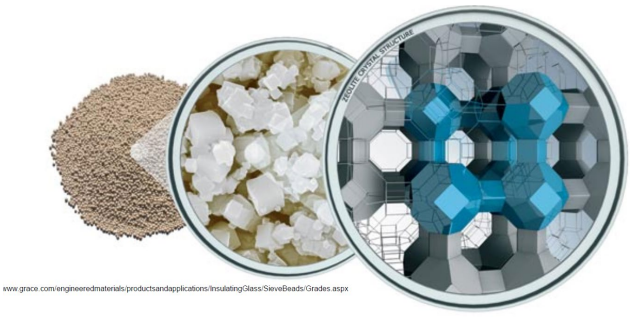


Figure 2. Zeolite Structure and Synthesis to Pelletized Form [4]

B. Historical Use of Zeolites in Spacecraft

1. Skylab 2-Bed Molecular Sieve (2BMS)

The 2BMS architecture with zeolite sorbents, or Regenerative CO_2 Removal System (RCRS), was first flown on the Skylab space station [5,6]. It was the first regenerable open loop Environmental Control and Life Support System, venting CO_2 and H_2O to space vacuum as shown in Figure 3.

This Skylab system provided partial humidity control as a condensing heat exchanger (CHX) was also used. Each Skylab bed as shown in Figure 4 was packed with 10.35 lbs of Linde 13X zeolite and 7 lbs of Linde 5A zeolite. Zeolite 13X, with a higher affinity for water, was used as the first layer, or desiccant bed, and 5A as the second layer, or CO_2 removal bed. The nominal operation consisted of 15 minute adsorption and 15 minute desorption half-cycles. The

primary system operated without any hardware issues for three Skylab missions without any need to activate the backup system.

As zeolites preferentially adsorb water vapor over CO_2, periodic bakeout of the beds via internal heaters while exposed to space vacuum is required. Generally, 5-hour bakeouts were performed at the start of each Skylab mission [7]. Interestingly, no mid-mission bakeout was required during the longest (84 day) Skylab mission, even though the 2BMS had been qualified based on bakeouts at 28 day intervals [8].

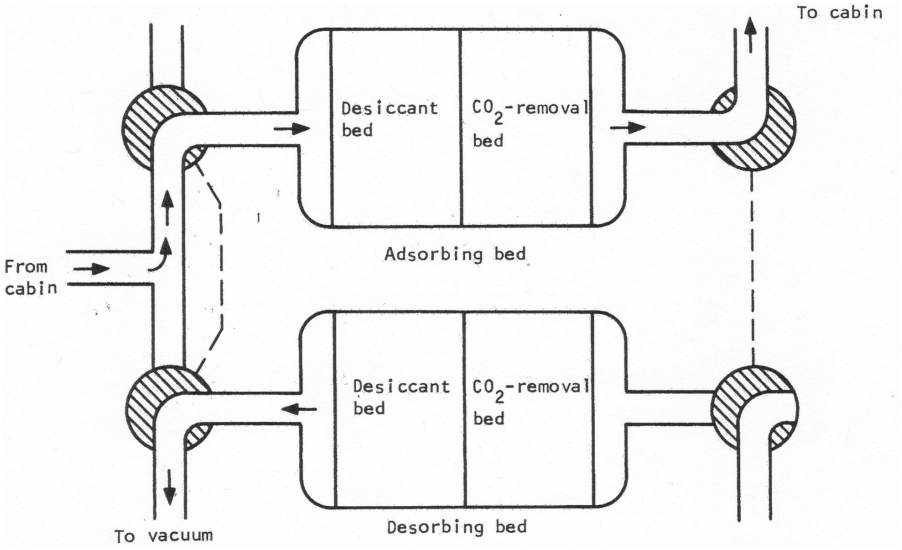


Figure 3. RCRS Schematic [9]

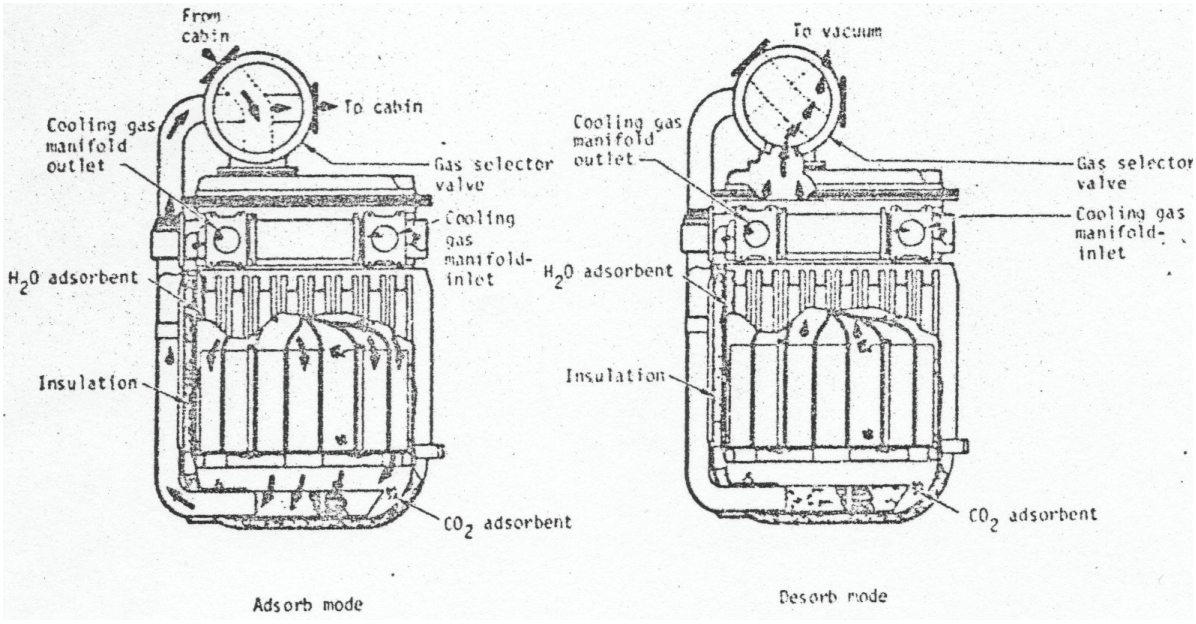


Figure 4. RCRS Sorbent Bed and Selector Valve [8]

No issues related to zeolite dusting were reported in the Skylab mission report [8], although the containment design used was functionally identical to that initially used in the ISS Carbon Dioxide Removal Assembly (CDRA). This design allowed zeolite dust and particles to escape between the spring plate and the bed (see Figure 8) with CDRA. Since the RCRS released CO_2 directly to space vacuum, zeolite escaping the bed may have simply vented to

space instead of clogging internal valves as with CDRA. The selector valve was of the plug valve type, using embedded seals, vs. the ball valve that proved problematic on CDRA. Since the RCRS valve design tends to wipe dust forward rather than embedding it into the seal, friction buildup on the seal would have been avoided. Another factor favored the RCRS with respect to zeolite dust issues; the total operation time on Skylab was only 171 days. A much longer mission time could have revealed, for example, dust obscuring the retention screen and reducing RCRS flow rate and efficiency. As the Skylab CO_2 removal efficiency was maintained throughout the mission, this did not appear to occur [8]. Unfortunately the lessons that could have been learned from either more extensive operational time or inspection of the hardware post-flight were lost when Skylab fell to earth in 1979. The first launch of the space shuttle program, delayed to 1981, came two years too late to reboost the Skylab space station as had been intended [10].

2. Carbon Dioxide Removal Assembly

The two CDRA [11] systems were launched to the International Space Station (ISS) in 2001 and 2010 as the primary atmospheric CO_2 removal devices. A schematic of this thermal-vacuum swing system is shown in Figure 5. The flight hardware is pictured in Figure 5. Beds 1 and 3 served to desiccate the air stream with silica gel and zeolite 13X prior to entering into the CO_2 sorbent beds. Water vapor captured in the desiccant beds is returned to the cabin for processing via a condensing heat exchanger and water recovery system. During nominal operation, the CO_2 captured by zeolite 5A in the CO_2 sorbent beds is virtually dry and can be either dumped overboard without loss of water, or fed directly to a compressor and downstream CO_2 reduction device without further desiccation.

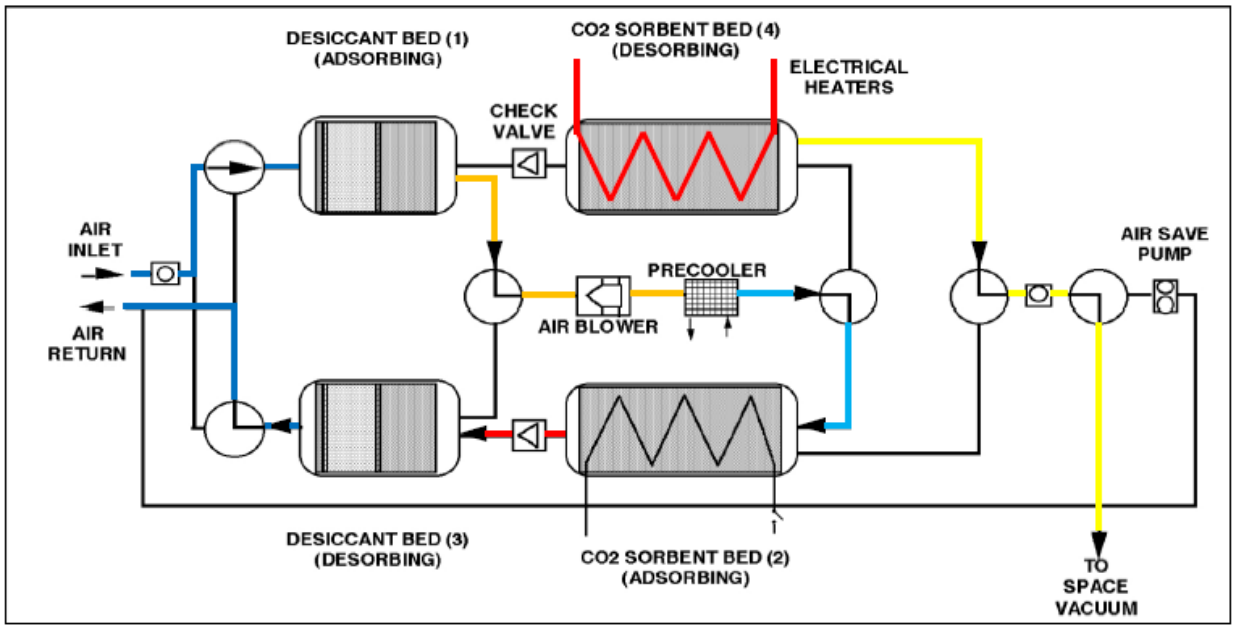


Figure 5. CDRA Schematic

The two CDRA systems provided the primary CO_2 removal function on the ISS for approximately 20 years. However, these systems had significant issues, most of which are attributed to design defects related to zeolite containment and the lack of dust mitigation features. This resulted in CDRA consuming the greatest amount of crew time for maintenance of any ISS system, and five redesign efforts were undertaken to address the outstanding issues. These issues are summarized below and will be further reviewed as countermeasures for these issues are discussed [12-14].

- Zeolite containment failure leading to component failures
- Rapid dust generation leading to screen blinding and high differential pressure across beds
- Sorbent selection based on standard industrial protocol inappropriate for spaceflight applications
- Bed design and filling procedures subject to unpacked voids leading to sorbent fluidization and attrition
- Selector valve design results in high velocity bed repressurization

These issues are further addressed in the design approach of the Sorbent-Based Atmosphere Revitalization (SBAR) system and the Four-Bed CO2 (FBCO2) Scrubber system as described in the following sections.

3. Sorbent Based Atmosphere Revitalization

SBAR [15] was developed as an Orion system risk mitigation technology. It is a vacuum-swing system similar in architecture to the Skylab 2BMS system, but includes patented enhancements that improve efficiency, reduce size, and extend the period between thermal bakeouts [16]. Between 2005 and 2014 SBAR was developed by NASA to an approximate Technology Readiness Level (TRL) of six. SBAR could provide humidity control for up to six crew for the Orion mission without requiring a CHX.

Figure 6 shows a schematic of the SBAR system. Virtually all H_2O is removed in the first zeolite 13X layer. CO_2 is removed primarily in the 5A layer. The blue process air line is shown with a partial bypass of the second section. Since crew H_2O loading is higher than CO_2 loading, the full flow is not required for the CO_2 removal section. Bypassing some of the flow extends the time period between thermal bakeouts. The red vacuum vent lines show three ports for vacuum venting. Using three ports has been shown to reduce overall bed pressure during desorption, resulting in more efficient desorption and thus greater adsorption on the subsequent half-cycle.

The SBAR system provides substantial improvements in mass, power, and volume compared to the Skylab CO_2 and H_2O removal system. A conceptual flight design of the SBAR system, including a primary and backup 2BMS unit, is shown in Figure 7.

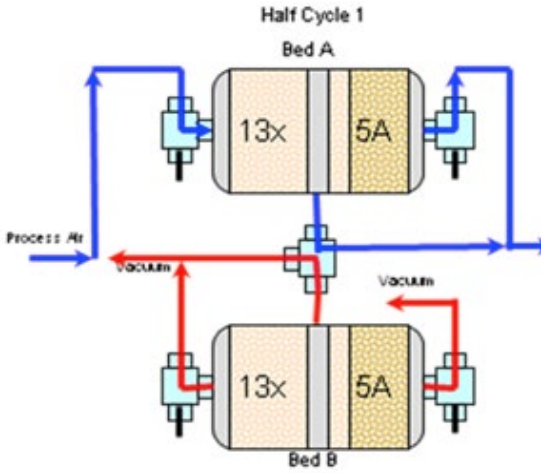


Figure 6. Sorbent Based Atmosphere Revitalization System Schematic

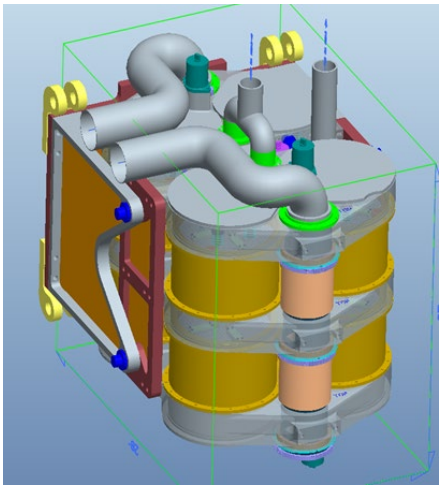


Figure 7. Sorbent Based Atmosphere Revitalization (Flight Concept)

The incorporation of cylindrical beds in the SBAR system was a significant improvement in zeolite dust retention and reduction in dust production. Both the Skylab RCRS and ISS CDRA sorbent beds are rectangular prisms, a shape that makes sense with respect to packing more sorbent in the limited spacecraft volume than cylindrical beds traditionally used in the chemical processing industry. However, drawbacks to the rectangular cross-section of these beds became apparent shortly after CDRA activation.

The first failure of CDRA was due to a lack of containment of zeolite in the packed bed. Due to the rectangular cross-section, the sharp corners did not allow for a simple O-ring seal to be used. The (room-temperature vulcanizing) RTV sealant approach used initially failed and allowed zeolite dust and particles to escape between the spring plate and the bed shown on the left of Figure 8. Although essentially the same design was used for the Skylab sorbent beds (though without RTV sealant), the escaped dust would vent directly to space. Unfortunately, in CDRA, the dust and partial pellets lodged in the air-save vacuum pump and seized it, shutting down CDRA. In addition, the check valves situated between desiccant and sorbent beds in CDRA developed leaks and selector valves failed due to sorbent contamination of sealing surfaces.

The containment redesign, also shown in Figure 8 (right side), incorporates a large O-ring between the spring plate and an insert for positive sealing. Additionally, a static secondary screen was added in the canister lid to ensure containment [14]. However, this design requires an insert (the outermost part in the right photo in Figure 8) that leaves a section of the zeolite underneath it unpressurized by the spring plate. This section is also difficult to fully pack with

zeolite as it is off to the side. These combined conditions have the potential to allow a void space that is subject to zeolite fluidization and rapid attrition. Note that the photos in Figure 8 were taken prior to operation and dust buildup.

Another issue was noted with the rectangular prism geometry. With this bed design, the flat bed walls tend to flex inward during depressurization in the beginning of the desorption step. During ground testing of systems, a crunching sound that was observed by one of the authors during the bed depressurization, likely due to zeolite crushing as the sorbent beds constricted.

Figure 9 (left photo) shows the SBAR containment design. By employing cylindrical beds, containment is achieved via a simple O-ring channel, with the O-ring riding directly on the sorbent bed canister. In this design the spring plate exerts pressure on the entire cross sectional area, and there are no obscured areas difficult to pack.

The photos in Figure 9 were taken after 1500 hours of operation (much more than intended mission durations on Orion, though only a fraction of a Mars transit vehicle mission duration) [15]. Some very fine dust can be observed on the edges of the cover and spring plate. This dust had passed through the 50 micron openings in the retention screen. Since the ball valve allows rapid depressurization, a short pulse of high velocity air passed through the screen every half-cycle, potentially causing attrition that resulted in the observed dust production.

The SBAR concept is currently under further development under the Marshall Space Flight Center (MSFC) FY25 Technology Innovation and Development funding. The objectives are to mature the SBAR system to be more competitive for short term missions, such as Gateway Airlock and lunar initial Surface Habitat by obtaining test data on the enhanced SBAR test unit to verify performance predictions and optimization of key performance parameters (KPPs). KPPs include operational lifetime, CO_2 and humidity removal rates, mass, power, and volume.

One key objective in the current effort is to enhance the SBAR design based on the design features developed for the FBCO2 Scrubber, including incorporation of the FBCO2 Scrubber internal bed heaters and valves that eliminate rapid depressurization. As discussed below, these features contributed to the success of FBCO2 in eliminating failures due to dusting to date.

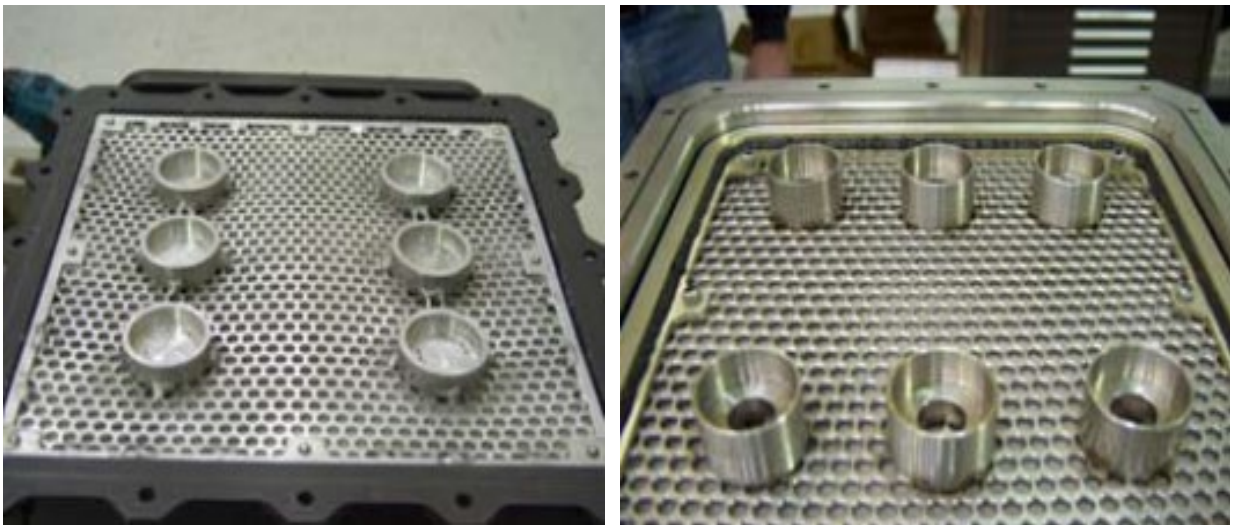


Figure 8. Failed CDRA Containment Design vs. Containment Redesign. Photo Credits NASA MSFC.

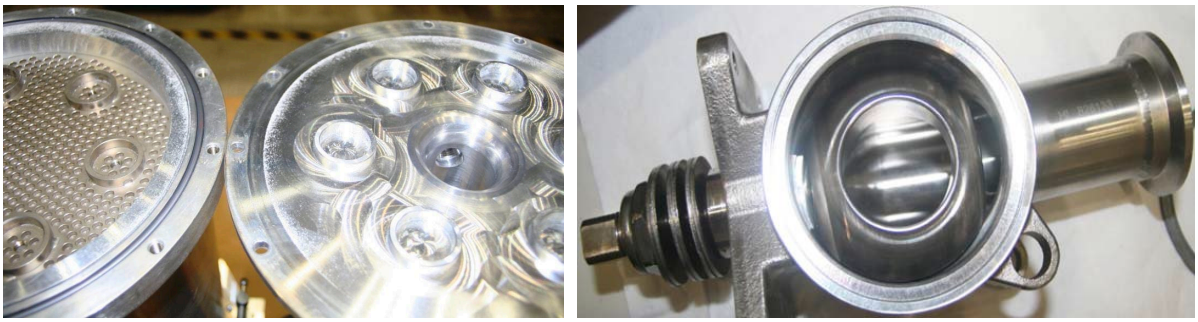


Figure 9. SBAR Containment Design and Valve [15]. Photo Credits NASA MSFC.

4. Four-Bed CO2 Scrubber

The FBCO2 Scrubber was developed as a technology demonstration to evaluate its potential as a CO_2 removal technology for advanced exploration systems. FBCO2 is a four-bed molecular sieve system that uses thermal and vacuum swing adsorption to scrub CO_2 by utilizing a 13X zeolite sorbent with water and air save capabilities.

Activated in September 2021, FBCO2 achieved 3 years of operational run time as of late February 2025 with minimal unplanned maintenance events. Due to its on-orbit performance and reliability, FBCO2 is operated as much as possible to reduce the use of heritage CDRA systems, playing a vital role in atmospheric revitalization for the ISS. The ISS Program is planning for the continued use of FBCO2 at 100% duty cycle through the end of ISS life in 2030.

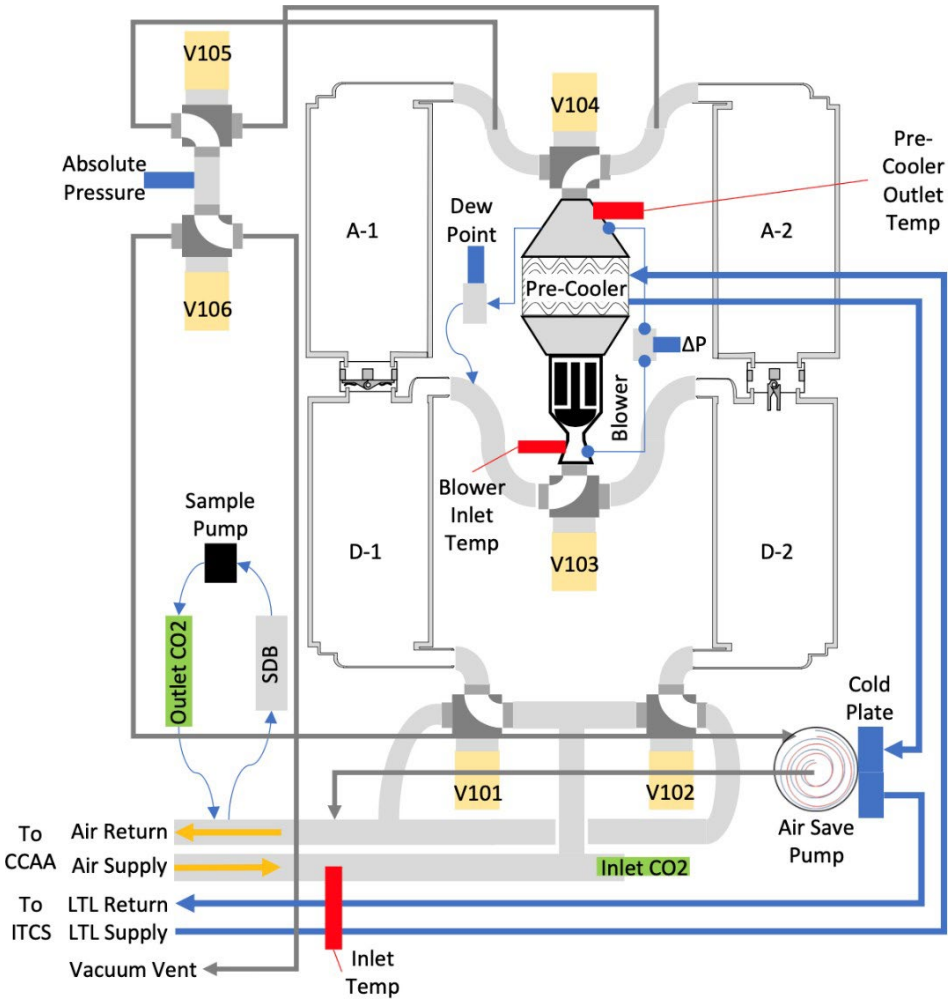


Figure 10. FBCO2 Scrubber Flight Hardware Diagram

A diagram of FBCO2 is shown in Figure 10 above. Core features and functions of the system have been described in greater detail in previous papers [17-19]. In summary, conditioned air from the Common Cabin Air Assembly (CCAA) is drawn into FBCO2 by the suction generated by the air blower. Four of the six air selector valves (ASVs) direct the air flow path. For Half Cycle A (HC-A), the flow path is through desiccant bed D-1, then adsorbent bed A-2, and finally through desiccant bed D-2 before returning the air to the CCAA. Water vapor is captured in bed D-1, and then CO_2 is captured in adsorbent bed A-2. Bed A-2 is hot from the previous cycle and that heat is used to push moisture out of bed D-2. HC-B operates symmetrically, with the beds changing from adsorbing to desorbing. The remaining two ASVs connect bed A-1 to an air save pump for 10 minutes and then to space vacuum for the remainder of the HC. The sorbent bed is heated to provide a thermal driving force for CO_2 to desorb and vent. Sorbent bed

heating is achieved by embedded heaters controlled to a setpoint temperature via internal resistance temperature detectors.

Although much of the architecture of the FBCO2 Scrubber is the same as CDRA, there are significant differences in sensors and components. FBCO2 includes additional sensors, including an inlet and outlet CO_2 sensor, inlet flow meter, and desiccant bed outlet humidity sensor. A scroll pump replaces the CDRA two-stage sliding vane air save pump. As discussed below, the FBCO2 selector valves were specifically designed at Marshall Space Flight Center to both be dust tolerant and help mitigate zeolite attrition due to rapid sorbent bed repressurization, and was awarded a patent in 2019 [20]. Finally a removable retention screen was included in the sorbent bed for rapid cleaning or inspection, which, as discussed below, was performed in 2024.

II. Detailed Approach to Dust Mitigation for the Four-Bed CO2 Scrubber

A. Overview of Approach

The issues associated with the heritage ISS zeolite-based system, CDRA, highlighted the need for mitigation of the zeolite dusting experienced over more than 20 years of CDRA operation. The initial effort at MSFC was focused on the selection of a structurally robust sorbent to replace the UOP RK38 zeolite after it demonstrated accelerated dusting in CDRA on the ISS. This scope was broadened when, in early 2014, the ISS Program Manager requested that the NASA ECLSS Systems Maturation Team review all possible alternate technologies and provide a recommendation to the ISS Program to guide decisions relative to next steps for CO_2 removal [21]. One alternative focused on at the Marshall Space Flight Center was a redesigned 4-bed molecular sieve, with the same architecture and similar or better CO_2 removal performance as CDRA, but without the zeolite related issues that resulted in extremely high maintenance requirements for that system.

The root causes for zeolite-related issues were identified and addressed systematically. Each root cause was addressed fully, as it is not possible to isolate a single cause that dominated dust production; the observed dusting could easily be caused by numerous factors. These root causes and the remediation steps taken are described below.

B. Areas of Focus

1. Ensure sorbent is fully contained in packed bed

As described in section IB3, Sorbent Based Atmosphere Revitalization, the conversion from cylindrically shaped sorbent bed (vs. the rectangular pyramid used for the Skylab CRCS and ISS CDRA) allowed for a simple O-ring seal to be employed without inserts that opened the potential for voids in the packing. No evidence of containment issues have been found for FBCO2.

2. Select strongest sorbents for system operating conditions

As mentioned above, a key issue with CDRA was rapid dust generation leading to screen blinding and high differential pressure across beds. When the differential pressure sensor approached its high limit, the sorbent beds initially had to be removed from the system and replaced with new beds. Later, a redesign enabled inflight screen replacement; however this process required a complete disassembly of the CDRA and was very time consuming, contributing to CDRA becoming the system requiring more maintenance than any other ISS system.

Various root causes for rapid dusting are plausible, including crushing under excessive spring loads, attrition due to development of voids, softening of pellets due to water vapor exposure, and accelerated attrition due to high velocities during bed repressurization.

Along seeking mechanical countermeasures for these root causes, the most robust sorbents were sought to minimize dusting as diminished but not zero stress conditions were likely to be attained. The process of seeking robust sorbents is addressed first below.

An extensive review of available commercial zeolites and silica gel sorbents was conducted at MSFC to identify both the structurally strongest and highest capacity sorbents [22-25]. Testing included pellet and bulk crush testing, hydrothermal stability testing, attrition testing, and CO_2 capacity testing as shown in Figure 11. The test protocol was adapted from industrial standards, but customized to more closely match the conditions in a 4BMS system. For example, crush and attrition was conducted at three humidity levels which are the upper and lower bounds, along with the midpoint, for the CO_2 adsorbent bed. The influence of humidity on sorbent strength and attrition is obvious in the results, yet for industrial protocols, no control over humidity is exercised.

The hydrothermal stability testing was a uniquely developed at MSFC, including thermal swings mimicking the adsorbent bed thermal experience. The test results correlated strongly with ISS experience. The sorbent with the

highest dusting rate on ISS, UOP RK38 5A, demonstrated the poorest hydrothermal stability as shown in the upper righthand graph, yet it had been selected to replace the obsolete UOP ASRT 5A based on industrial testing protocol.

Grace Davison Grade 544 zeolite 13X was selected as for the FBCO2 Scrubber CO_2 adsorbent bed based on overall superiority in strength, attrition resistance, hydrothermal stability, and CO_2 capacity. Another factor was proven superior performance as a residual desiccant in the CDRA desiccant beds.

Desiccants were also tested. In this case the current CDRA desiccants, including Grace Davison Grade 544 zeolite 13X, were found to be superior to alternatives, and thus used in the FBCO2 Scrubber.

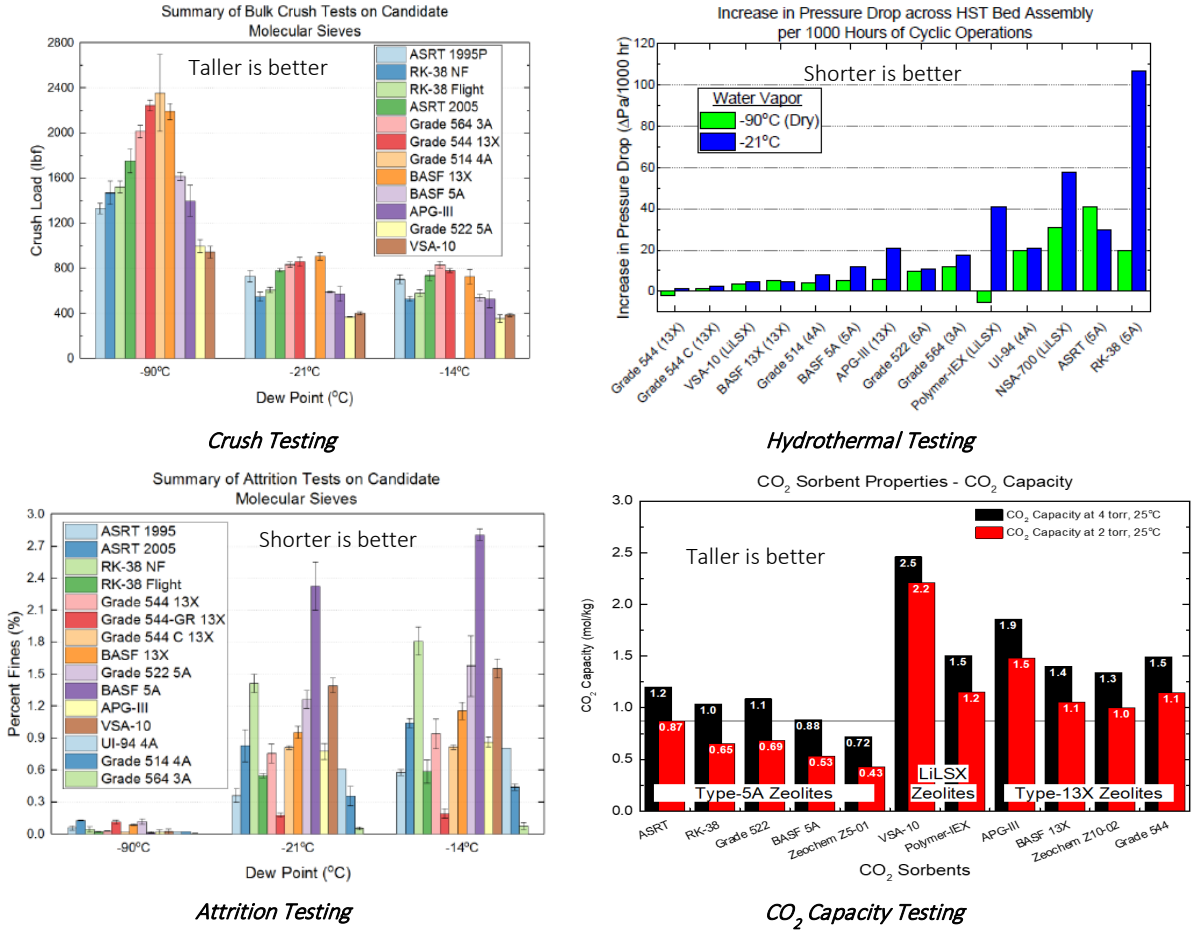


Figure 11. Sorbent Characterization Testing Results [22-25]

3. Eliminate high velocity airflow during valve transition

The use of ball valves to repressurize the sorbent bed after being at vacuum is likely to lead to high velocity flow encouraging sorbent attrition. This results from the large flow area of the valve during transition to the new port. The ball valves employed by CDRA and SBAR are suspected to have contributed to the production of zeolite dust observed in both systems.

The FBCO2 air selector valve was specifically designed to reduce flow velocity via a small diameter "bleed port" used during bed repressurization [25]. The flow velocities experienced by sorbents in CDRA using a standard ball valve and of a valve with a bleed port to moderate flow velocities are shown in Figure 12. Also shown is an industry standard allowable velocity as horizontal line. As shown, CDRA velocity greatly exceeds the industry limit, while the velocity with the modified valve used by the ground test Linus 4BMS remains below that line. The MSFC developed air selector valve used in the FBCO2 Scrubber reduced flow velocities below the industry standard limit, resulting in reduced attrition and reduced dust generation in CO_2 adsorbent beds.

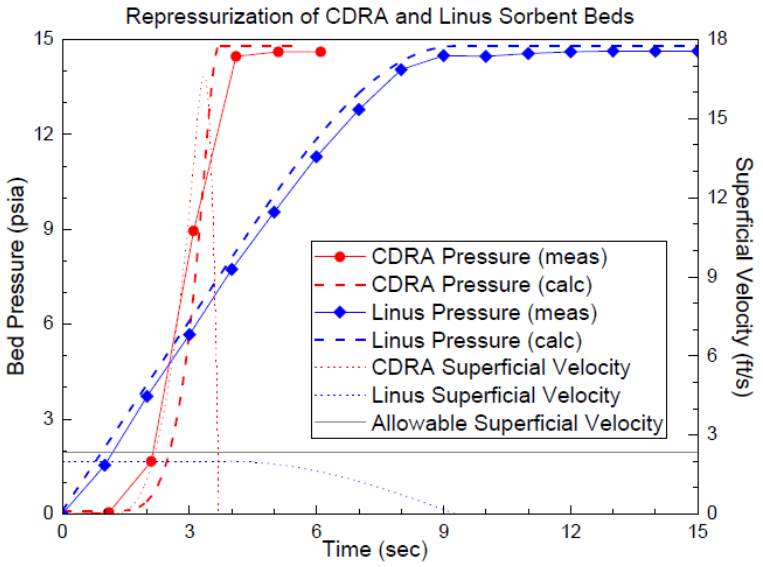


Figure 12. Repressurization of CDRA and Linus Sorbent Beds

4. Enable visual feedback during sorbent packing to avoid voids

The CDRA heater core design is shown on the left side of Figure 13. Sheet heaters (seen in beige) are used to along with aluminum sheet metal heat spreaders to desorb the zeolite. Due to the small channels as well as rods used to hold the heater core together (not visible) it is not possible to view the sorbent during packing. As a result, the sorbent tends to "log-jam" or bind during packing leaving undiscernible gaps below the log-jam. Resulting voids allow fluidization of zeolite pellets and rapid attrition.

The FBCO2 heater core is shown on the right side of Figure 13. An open design was chosen to ensure full visibility of the sorbent during the packing process and thus avoid creation of voids. This design is also being incorporated in SBAR.

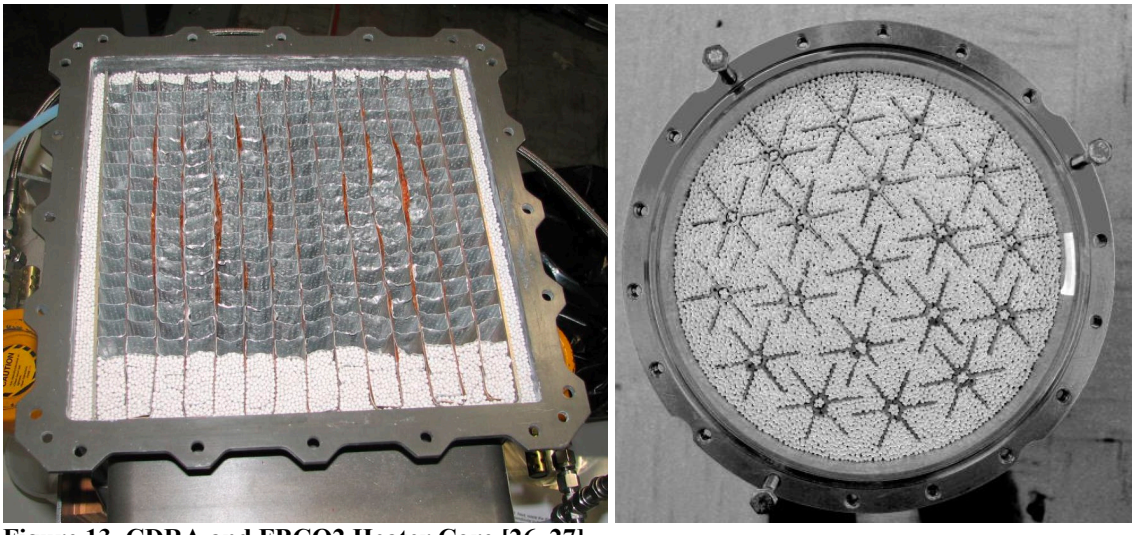


Figure 13. CDRA and FBCO2 Heater Core [26, 27]

5. Ensure compacting force will not crush weakest pellets

Springs are used to maintain compaction of sorbent. Pellet crush tests reveal a distribution of crushing force, showing that some pellets crush under forces five times lower than the average crush strength. Thus the objective is to minimize applied pressure to protect the weakest pellets. A re-evaluation of required force considering O-ring squeeze and launch loads was conducted. This analysis allowed for a 50% reduction for FBCO2 Scrubber spring force compared to the CDRA spring force, reducing applied pressure from 10 to 5 psia.

6. Apply compaction throughout to avoid loosely packed regions

As a byproduct of the redesign of the CDRA retention approach, it was found that the rectangular design prevents zeolite compaction in corners, possibly leading to flow blockages requiring maintenance after as little as 6 months of operation. The beds in the SBAR and FBCO2 Scrubber both have circular cross sections which enables full compaction. This was described in greater detail in section IB3, Sorbent Based Atmosphere Revitalization.

III. Observed Results

The SBAR system employed only the subset of the dust remediation steps appropriate to its operation, as it does not experience frequent thermal swings. This system revealed minimal dust after 1500 hours of operation.

The FBCO2 Scrubber was designed with all dust remediation steps. Ground tests of over 1000 hours yielded 0.01 gram of dust collected, a small fraction of that observed with CDRA. However, flight results were even more telling. In early 2024, the adsorbent bed filters were removed to verify the effectiveness of the design updates used to mitigate the recurring zeolite dust problems seen in CDRA. The ISS crew noted the screens looked visibly clean with very minimal dust liberation coming from the screen. A photo taken after removal is seen in Figure 14 below.



Figure 14. Adsorbent bed filter from FBCO2 Scrubber in the U.S. Laboratory Destiny

Both filters were returned on the SpaceX Cargo Resupply Services Mission 30 flight in April 2024 and were analyzed by Boeing at the Huntsville Central Laboratory for particle size fractioning, particle identification, and contaminant loading. Analysis showed the filters had little to no debris on the filters themselves and the majority of the dust was found in the sample bag they were returned in. The total mass of dust debris, which contained some contaminants thought to be from the vacuum collection adapter, was 0.03 grams. In comparison to a previous CDRA dust analysis performed in 2014, FBCO2 dust production was found to be reduced by 2 to 3 orders of magnitude over a 2-year operational period. The particles were found to mainly consist of sodium aluminosilicates, which is the chemical composition of zeolite 13X. The zeolite dust size ranged from 5-59 μm, with larger particles up to approximately 750 μm lodged in the screen.

To gather additional information on the effectiveness of the dust remediation techniques, including whether attrition rates remain approximately linear overtime, another FBCO2 filter replacement is being targeted for early 2027.

IV. Conclusion

The efforts undertaken in 2014 to eliminate the issues associated with zeolite dusting observed with the ISS CDRA, yet utilizing the excellent demonstrated performance of CDRA, have been successfully met. This paper has reviewed those issues, the remediation efforts researched and implemented by the team at MSFC, and the evidenced success of those design changes on the FBCO2 Scrubber. These lessons learned will be applied to future zeolite systems such as the SBAR if selected for future Lunar and Mars missions. Notably, these successes translate into both cost and mass

savings, as the need for crew maintenance time is significantly reduced and fewer on-orbit replacement units are needed for sparing.

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