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A long-term goal for NASA is to enable crewed missions to Mars: first to the vicinity of Mars, and then to the Mars surface. These missions present new challenges for all aspects of spacecraft design in comparison with the International Space Station, as resupply is unavailable in the transit phase, and early return is not possible. Additionally, mass, power, and volume must be minimized for all phases to reduce propulsion needs. Mass reduction is particularly crucial for Mars surface landing and liftoff due to the challenges inherent in these operations for even much smaller payloads. In this paper we describe current and planned developments in the area of carbon dioxide removal to support future crewed Mars missions. Activities are also described that apply to both the resolution of anomalies observed in the ISS CDRA and the design of life support systems for future missions.

Nomenclature

CDRA = Carbon Dioxide Removal Assembly
HEO = Human Exploration and Operations
ISS = International Space Station
LSS = Life Support Systems
NASA = National Aeronautics and Space Administration

I. Introduction

NASA’s Human Exploration and Operations (HEO) directorate includes the Advanced Exploration Systems program, which has the charter of “pioneering new approaches for rapidly developing prototype systems, demonstrating key capabilities, and validating operational concepts for future human missions beyond Earth orbit. AES activities are uniquely related to crew safety and mission operations in deep space, and are strongly coupled to future vehicle development.”¹¹ The efforts described herein are part of the Life Support Systems (LSS) project under AES as shown on the HEO website: “The AES program consists of about 20 small projects that target high-priority capabilities needed for human exploration such as advanced life support... Early integration and testing of prototype systems will reduce risk and improve affordability of exploration mission elements. The prototype systems developed in the AES program will be demonstrated in ground-based test beds, field tests, underwater tests, and flight experiments on the International Space Station (ISS).” In this paper, efforts to develop CO₂ Removal technologies (part of a life support system) for Exploration missions are described. These efforts are focused on producing two ISS

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flight experiments. 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.

II. 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 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. This scope was broadened when, in early 2014, the ISS Program Manager requested that the NASA 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.

In response to this request, two technical interchange meetings (TIMs) were held in the spring of 2014. NASA life support personnel met in March 2014 to review ISS CDRA issues and emerging medical concerns with current spacecraft CO$_2$ concentration limits (which are approximately 10X earth normal concentrations). NASA sponsored development work and alternate technologies known at that time were also discussed. The criteria and goals for Exploration CO$_2$ removal systems were discussed, and plans were made for a follow-on workshop that would include industry, other government agencies, and academia.

In April 2014, the follow-on workshop was held with a broader group. Ten non-NASA organizations participated, including NAVSEA, six commercial entities, and three academic groups. These organizations were briefed on CDRA issues, medical concerns, and ongoing NASA efforts. Most organizations, in turn, briefed NASA on their potential contribution to CO$_2$ Removal technology development. In a follow-on session, the Department of Energy also provided a briefing on their activities in CO2 Capture and Storage (CCS).

The information gathered at these TIMs was used to develop a proposed roadmap, which is shown in Figure 1. The long-term goal is to develop two technology demonstrations, or flight experiments, 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. One of the technology demonstrations would be based on the current ISS CDRA, with improvements in reliability and performance. The second would be selected from other promising technologies after further development as required to bring the candidates to similar technology levels. In addition to developing the technology demonstrations, this effort would provide recommendations for hardware and sorbent upgrades for the ISS CDRA.

The proposed approach was presented to the Space Station Program Control Board (SSPCB) in August of 2014 to confirm that the general plan was acceptable prior to developing a full cost estimate. In October of 2014 the revised approach was presented to the SSPCB and approved. At the end of the second quarter of FY15, funding was provided from the ISS program to the appropriate NASA field centers. This funding, combined with prior AES LSS and ISS funding, is to enable full implementation of the roadmap in the near term. Funding requirements for the long term are not yet defined as they are dependent on future technology selections. In the following sections, the details of the approach and a summary of recent work is presented.

III. Approach

Three principle goals of the CO2 Removal Roadmap are listed below:

1. Select superior desiccants and CO$_2$ sorbents for ISS CDRA. Criteria for selection includes performance, structural stability, and sensitivity to contamination. Only sorbents compatible with the current ISS CDRA hardware are under consideration.

2. Using the ISS CDRA design as a basis, complete design of a next generation CO$_2$ removal system with appropriate attributes for a 2-year mission with no resupply. Implement this design in the fabrication of a technology demonstration to fly on ISS by 2019.

3. Down-select between promising alternate technologies after further development as required to bring the candidates to similar technology levels. Complete design of a next generation CO$_2$ removal system based on the selected technology with appropriate attributes for a 2-year mission with no resupply. Implement this design in the fabrication of a technology demonstration to fly on ISS by 2019.

All three goals require accurate selection of the superior sorbent (zeolite, silica gel, alumina, solid amine, etc.). However goals 2 and 3 also require selection of the superior process (four-bed molecular sieve [4BMS], CO$_2$ Removal and Compression [CRCS], rapid cycle pressure swing adsorption [PSA], etc.) coupled with the superior sorbent format (clay-bound pellets, polymer-bound monolith, honeycomb monolith, sorbent coated metal, etc.).

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Figure 1. Recommended Roadmap for CO₂ Removal. Green tasks are funded under ISS or AES; Yellow tasks are partially funded, and red tasks require new funding.

### A. Structural Stability
Sorbent structural stability must be considered in selection of a superior sorbent. A high rate of attrition results in increases in fixed bed differential pressure as dust builds up on particle retention screens, increasing the blower power required to maintain flow and eventually requiring astronaut maintenance, which is highly undesirable. Dust fines propagate downstream and can accelerate failure rates in downstream components. Data from a series of particle characterization tests performed in dry and humid conditions, including pellet crush strength, bulk crush strength, attrition, and hydrothermal stability are being compiled and correlated for use in sorbent selection and process design. For example, structural sensitivity to moisture will dictate the allowable content in a CO₂ sorbent bed influent stream, thus restricting the desiccation process parameters.

### B. Sensitivity to Airborne Contamination
Degradation of sorbent performance and structural stability due to airborne contaminants must also be considered in the selection of a superior sorbent. It has been observed that long-term (approximately one year) exposure to the International Space Station atmosphere results in significant losses in silica gel water vapor capacity. Capacity losses may occur in other sorbents as well; testing is ongoing to make these determinations. Tests include working capacity testing via TGA, surface area analysis, particle size distribution, misting studies, and contaminant loading via GC/MS. The results from these tests are being compiled and correlated. As sufficient data becomes available, end-of-life sorbent characteristics will be used in the process models and process performance evaluation.

### C. Performance Optimization
The fundamental performance aspects of many sorbents (such as surface area, equilibrium working capacity, and selectivity) have been used as metrics in order to rank their potential superiority in a particular application. However these metrics can provide conflicting data regarding which sorbent is superior, and have been shown to be unreliable in predicting superiority in process performance for Post-Combustion CO₂ Capture.

For spacecraft CO₂ Removal, an equally complex application, standard figures of merit alone will not be used to optimize the processes involved. Rather, computer simulations that capture the key physics of the process, including coupled heat and mass transfer in porous media, must be applied. A large number of parametric simulations (also
referred to as virtual tests) are required to converge on the optimal solution. Parametric hardware testing could also be employed of course, but would be prohibitively expensive and time-consuming, severely limiting the number of options that can be explored.

A 1-D computer model has been developed recently and will be used for parametric virtual testing at a fraction of the cost and time required for hardware test development and execution. The 1-D model of the ISS CDRA was constructed using the COMSOL® Multiphysics code. Built-in COMSOL® modules for chemical transport, Darcy flow, and thermal transport were used to solve for concentrations, pressures, and temperatures, respectively. Each one of the four beds is modeled as a separate domain with its own physics nodes, boundary conditions, and solver settings. Within each of these domains, the temperature of the sorbent, gas, and surrounding canister is determined through separate heat transfer nodes. Domain PDE nodes are used to solve for the local pellet loading. This model is currently undergoing multi-point validation against a CDRA ground test unit. Modifications of this model will be made to simulate other processes, however, as most adsorption processes under consideration (temperature swing adsorption, vacuum swing adsorption, and hot purge desorption) are present in the CDRA, modifications may not be extensive. Early results from validation are shown in Figure 2. Please refer to Ref. 9 for more details on this model and simulation results.

![Figure 2. Comparison of simulation and test results: temperatures at the heater TC locations in the sorbent beds (left) and partial pressure carbon dioxide at the desiccant bed influent and effluent (right).](image)

Other aspects of sorbents including structural stability under humid conditions and sensitivity to airborne contamination are also important to successful long-term operation. Since planned exploration missions such as transit to Mars and back to Earth require approximately two years of operation without resupply these long-term effects must also be evaluated.

In Figure 3 the integrated optimization approach is shown. This process will be applied to the Improved CDRA Path and the Alternate Technology Path independently. Essentially there are three steps in performance optimization: the first to screen out the worst performing sorbents, the second to obtain the “Startup Performance Optimization” and the third to obtain the final “Ranking of Sorbent/Process Systems”.

In the second step, sorbent and process characteristics are determined and simulated. Process parameters such as bed sizes, flow rates, cycle times, etc. are varied in a series of virtual tests in order to optimize the performance of each candidate process and sorbent combination. The top performing combinations are subjected to hardware testing to confirm results and validate the simulation. If required, simulation refinement and hardware test are repeated until validation is successful. Upon completion of this step, the optimal process, sorbents, and process parameters have been determined based on the characteristics of unused sorbents. This is the “Startup Performance Definition” in Figure 3. The number of sorbent/process systems carried forward to step three will depend on their relative ranking at this point.

As the ISS CDRA as well as commercial experience has revealed, long-term operation can lead to sorbent degradation including capacity losses and attrition. These factors will be accounted for in the third step, where a second round of parametric virtual testing is conducted. As different sorbents have varying sensitivities to contamination and varying long-term stability, the initial ranking may change when end-of-life performance, flow losses, and maintenance requirements are factored in.
A full-scale hardware test article, or engineering development unit (EDU), based on the top ranking sorbent/process system will be fabricated and tested. More than one system may be tested depending on the closeness of the ranking, especially if the systems are similar enough that only minor changes to the hardware are required.

The final deliverable from this process is a technology demonstration system to be flown as a flight experiment on the ISS. The technology demonstration system will be largely based on the EDU, but incorporate lessons learned in the full-scale testing.

Figure 3. Integrated Optimization Approach Flowchart

IV. Status of Ongoing Tasks

An overview of many of the active tasks on the CO₂ Removal Roadmap is provided in the following sections. References to papers dedicated to each topic is provided for more detailed information.
A. CDRA-4EU Ground Testing with Optimized Half-Cycle Time and Flow Rate

Under the ARREM project and ISS program, a 4-Bed Molecular Sieve (4BMS) system, the CDRA-4 Engineering Unit (CDRA-4EU) was developed to more closely mimic the International Space Station (ISS) CDRA-4, and thus provide a better understanding of the state-of-the-art system performance and limitations. The objective for this task is to optimize the CDRA operational configurations such that exploration goals are met while increases in power requirements are minimized. In support of this effort, initial baseline testing with the CDRA-4EU was performed to provide pre-requisite source data for computer model refinement and to provide baseline data for comparison with future testing.

Minimizing power requirements of life support processes is a high priority for space flight, especially for long-term missions where there is limited availability. In order to understand the CDRA power usage during various runtime configurations, a set of test parameters were developed. Flow rates in increments of 8.5 m³/hour (5 SCFM) were chosen. Approximate cycle time for stoichiometric breakthrough was calculated for 2, 3, and 4 mmHg inlet partial pressure CO₂ at each selected flow rate for the CDRA-4EU. Cycle time for each data point was determined at the time when 50% breakthrough was predicted to occur.

Performance optimization was also sought for the above test points. The half-cycle time for the power optimization runs were set at the time that breakthrough of CO₂ was just beginning.

A subset of the test results is shown in Figure 4. This data provides insight into optimization of the CDRA power and efficiency for a range of flow rates and CO₂ partial pressures, as well as the baseline data for CDRA simulation validation. Selected removal rate data, for cases with CDRA inlet partial pressure controlled to 3 torr, are shown in Figure 5. This figure also shows, as light blue points, the estimated removal rates based on a Minitab correlation. Although the correlation is reasonable when used for interpolation it has questionable consistency when used for extrapolation. It is anticipated that the 1-D CDRA simulation will provide a predictive capability as needed for design optimization where testing is not practical. Further details on this CDRA-4EU testing may be found in Ref. 10.

B. Sorbent Pellet Screening and Characterization

Although pellet attrition cannot be completely eliminated, experiences from commercial and spacecraft life support operations and testing has shown that some sorbents are less susceptible to attrition. If attrition rates can be minimized, loss of flow can also be minimized and maintenance needs eliminated or greatly reduced. Also, identification of specific causes for structural weakness, such as humidity or temperature thresholds above which attrition is accelerated, can help guide future system design.

The structural integrity of candidate sorbents is being determined by three tests based on ASTM standards: single pellet crush strength, bulk crush strength, and attrition tests. These tests are conducted with very dry sorbents as well as with the sorbents conditioned to three humidity levels as shown in Table 1. Hydrothermal stability is being determined via a unique test that mimics the CDRA temperature profiles during desorption. Four columns are used for each sorbent to expose it to four different adsorption humidity levels.
Figure 5. Surface Plot of Removal Rate vs. Inlet Flow and Half Cycle Time for cases with inlet CO$_2$ partial pressure of 3 torr. Test data points are shown in dark blue; results based on a correlation are shown in light blue.

Table 1. Humidity Levels Used In Sorbent Tests

<table>
<thead>
<tr>
<th>Inlet Vapor Pressure (mmHg)</th>
<th>Dew Point Temperature (°F)</th>
<th>Dew Point Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.25E-05</td>
<td>-130</td>
<td>-90</td>
</tr>
<tr>
<td>0.012</td>
<td>-71</td>
<td>-57</td>
</tr>
<tr>
<td>0.70</td>
<td>-6</td>
<td>-21</td>
</tr>
<tr>
<td>1.38</td>
<td>7</td>
<td>-14</td>
</tr>
</tbody>
</table>

1. Single Pellet and Bulk Crush Testing

Crush strength is measured both for single pellets and in a small packed bed for the Bulk Crush test. Pellet crush tests are performed in an electro-mechanical test frame as shown in Figure 6; here the pellet is crushed between the lower and upper platen. Pellet and bulk crush tests are being conducted in the dry state per ASTM D4179 and D7048-04 respectively, and also with sorbents conditioned and maintained at two to three controlled moisture levels. Results as shown in Figure 7 have shown a clear correlation between moisture conditioning and reduction in crush strengths. In this figure, test results for two different lots of a zeolite 5A, UOP RK-38, are shown. “Flight RK-38” is material from a lot also used to pack the ISS CDRA currently in Node 3. “Non-Flight RK-38” is from a separate lot not used to pack the ISS CDRA. “ASRT 1995P” is zeolite 5A from a custom lot prepared specifically for use in the ISS CDRA in 1995, and also used in the MSFC Performance and Operational Issues System Testbed (POIST) 4BMS$^{13}$.

Bulk crush testing is conducted in the test article shown in Figure 8. The piston is subjected to a pre-determined load for 30 seconds in an electro-mechanical test frame, and resulting fines separated by sieving. The crush strength is defined as the value that produces 1% of fines by weight. Sample data is also shown in Figure 8; here the value for 1% fines is interpolated from a minimum of six data points.

Since the single pellet tests require less time and much less sorbent, but are less representative of the actual process than the bulk crush test, work is underway to develop a correlation that could be used to screen sorbents with pellet crush strength test results alone. Early results are encouraging; Figure 9 indicates that normalized data provides a
reasonable correlation in general between the pellet crush strength and bulk crush strength. More data is required to determine if the results shown for Flight RK-38, which does not correlate well, is an exception to the general trend. For additional information on the pellet and crush strength tests and results, refer to Ref. 11.
Attrition and abrasion testing is conducted per ASTM D4058-96, which calls for a cylindrical test cylinder as shown in Figure 10. Due to the internal fin, the sorbent pellets are lifted to the top of the cylinder and allowed to fall in each rotation. The test cylinder is rotated 1800 revolutions at 60 RPM in the Rotap device, also shown; the weight percent of fines produced is used to compare the attrition and abrasion of sorbents. As with the pellet and bulk crush tests, the sorbents were conditioned to varying levels of humidity as shown in Figure 11. For additional information on the attrition test and results, refer to Ref. 11.
2. Hydrothermal Stability Testing

During the ISS CDRA Temperature and Vacuum Swing Adsorption (TVSA) process, vacuum and heating is used to drive CO$_2$ off the zeolite pellets. Possibly due to the temperature swings, the CO$_2$ sorbent beds have always shown an increase in differential pressure over time. After repacking the Node 3 CDRA with zeolite RK-38, the increase in differential pressure became much more rapid. A possible contributing factor for this rapid increase is the introduction of humidity to the 5A zeolite due to leakage or from other causes. The Hydrothermal Stability Test was designed to understand the long-term influence of thermal swings in combination with varying levels of water vapor on the structural integrity of CO$_2$ sorbents.[14]

A simplified flow schematic for the test stand developed to implement the HST is shown in Figure 12. The test stand is configured with eight identical test beds that are paired to allow side-by-side testing of the two types of zeolite. For the initial testing, the 2 types of 5A zeolite under evaluation are zeolite RK-38, currently in the on-orbit CDRA, and zeolite ASRT that was in the CDRA previously.[12]
Figure 12. Schematic of Test Article Assembly

Figure 13 shows the pressure drop over the duration of Run 5. The test run lasted 1056 hours, which is the thermal cycle equivalent of ≈87 days of ISS CDRA operations. The plots show that, for the RK-38 material, there is clear correlation between the increase in pressure drop and the humidity of the process gas. Since the RK-38 and ASRT materials have different pellet shapes and packing characteristics, the initial pressure drop for the ASRT is nearly twice that of the RK-38. However, as the figure shows, there was minimal increase in the pressure drop across any of the ASRT beds. A numerical analysis of the data indicated that the increase in pressure was linear in nature and relatively constant over the duration of the run for all of the humidity cases. For additional information on the hydrothermal stability test and results, refer to Ref. 12.
Figure 13. Differential Pressure across Test Beds during 1056 Hour Run

3. Sensitivity to Airborne Contamination

A desiccant contamination sensitivity analysis has been performed on sorbent materials. These included sorbents returned from the ISS CDRA as well as those prepared in-house with the principle objective being evaluation of the degradation of sorbent working capacity due to contamination from the atmosphere of the International Space Station. Sorbents returned from the ISS CDRA were analyzed to determine (1) the contaminate loading and (2) the resultant loss of working capacity compared with fresh sorbents. In order to evaluate the sensitivity of candidate sorbents, the fresh sorbents were doped based on the above analysis of sorbents returned from the ISS CDRA, and their working capacity evaluated.

Figure 14 shows the result of tests conducted with a thermogravimetric analyzer (TGA) modified to allow sub-ambient temperatures and humid inlet gas. The difference in adsorbed mass of water between adsorption step (10C temperature and dew point) and desorption step (50C temperatures and approximately -90C dew point) as measured by the TGA, after equilibrium is reached, is the working capacity. As shown in the figure, working capacity losses, as compared to fresh silica gel, varied by sample. For the ISS samples at an approximate silica gel bed depth of 0.5 inches (samples 1-5 and 5-7), working capacity losses of approximately 45% and 60% were observed. The two ISS samples (1-8 and 5-9) at an approximate silica gel bed depth of 1.5 inches showed working capacity losses of approximately 25%. These results are consistent with greater amounts of contaminants being adsorbed closer to the inlet of the silica gel bed.

Fresh Grace Grade 40 silica gel was activated and doped with the siloxane observed in the highest quantity on the ISS samples based on GC/MS analysis. Liquid decamethylcyclopentasiloxane, or D5, was evaporated into an airstream before entering a small silica gel bed. This sample, “Activated Grade 40 with D5”, was found to have a working capacity loss of about 25%, or nearly that of the ISS samples at the 1.5” bed depth. This data indicates that the larger observed capacity loss in the samples near the silica gel bed entrance is a cooperative effect of multiple contaminants.

Forward work includes further refinement of the analog sorbent doping system to more closely meet on-orbit sample concentrations in conjunction with further testing of the Grade 40 and other comparable sorbent bed material such as Sylolbead SG B 125. Taken together these findings should be important in the understanding of contaminant uptake by sorbent bed materials and determining what threshold values may exist that could affect long-term bed sorbent performance. For additional information on contamination sensitivity tests and results, refer to Ref. 15.

Figure 14. Working Capacity of Fresh Silica Gel (Grade 40 Baseline), ISS Samples, and Doped Silica Gel (Activated Grade 40 with D5). Dry N2 gas at 50C temperature and approximately -90C dew point was used for the desorption step. Adsorption was conducted at 10C temperature and dew point.
C. CO₂ Removal and Compression System

The Carbon Dioxide Removal and Compression System (CRCS) is designed to perform both the Carbon Dioxide (CO₂) removal function of the four-bed molecular sieve (4BMS) system currently employed on the International Space Station (ISS), as well as additional integrated ability to thermally compress CO₂ to supply downstream CO₂ recovery units. The CRCS approach has the potential to reduce cost and improve reliability for future long-duration missions.

The CRCS consists of two concentric lightweight cylindrical cylinders made of stainless steel (SS) 316 material. The CRCS design drawings are shown in Figure 15. The inner cylinder represents the first stage where it is filled with zeolite 5A to adsorb CO₂. The outer gap of the cylinder is the 2nd stage where CO₂ is compressed and stored for delivery to the Sabatier reactor. For maximum heat transfer between the shared wall of stage 1 and stage 2, the stage 1 wall was fabricated as thin as possible with SS316 material.

The fabrication, assembly, and initial testing of the first of two CRCS test articles, the CRCSa, have been completed. Data from heating curves indicated that there is 120°C temperature variation from the center to the top and bottom of the heater coils in stage 1. The temperatures curves for stage 2 show that there may be issues with stage 2 not fully desorbing. At the time of this draft, no CO₂ was fed through the system. The CO₂ tests should be completed soon and data will be presented. Lessons learned from CRCSa will be applied to the fabrication and testing of the second test article where feasible within cost and schedule. For additional information on the Carbon Dioxide Removal and Compression System, refer to Ref. 16.

Figure 15. Design pictures of the CRCS showing the lids, heaters, and retaining screens.
V. Conclusion

Although the development of CO₂ Removal systems appropriate for extended exploration missions, such as to Mars, has been underway for many years, recent difficulties with the ISS CDRA system have underscored the importance of this work. The NASA System Maturation Team for Environmental Control and Life Support has been tasked with expanding and accelerating the CO₂ Removal development effort. In this paper we have presented an integrated approach to selection and optimization of CO₂ Removal systems for exploration missions. Included as part of this approach is the selection of superior sorbents for the ISS CDRA.

In this paper we have also provided an overview of many of the active tasks on the CO₂ Removal Roadmap. Results from many of these tasks provide information immediately applicable to sorbent selection for the ISS CDRA. All of the tasks in the roadmap will be applied towards the longer term selection of sorbents and systems for technology demonstrations on the ISS.

VI. References