Development of Carbon Dioxide Removal Systems for Advanced Exploration Systems 2015-2016

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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

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>CDRA</td>
<td>Carbon Dioxide Removal Assembly</td>
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<tr>
<td>HEO</td>
<td>Human Exploration and Operations</td>
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<td>ISS</td>
<td>International Space Station</td>
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<td>LSS</td>
<td>Life Support Systems</td>
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<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
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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.”¹ 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 ISS 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.

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II. Background

It is recognized by the life support community that the current ISS state-of-the-art CO₂ removal technology has reliability and capability gaps that must be solved both for ISS and future Exploration missions. From FY12 to FY14, the Atmosphere Revitalization Recovery and Environmental Monitoring (ARREM) project under the AES program included efforts to improve the CO₂ Removal state-of-the-art by seeking more robust sorbents and evaluating alternate sorbent formats and fixed-bed 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 CO₂ removal. This recommendation was to include goals for both ISS and future Exploration missions.

As reported on in a previous paper, technical interchange meetings (TIMs) were held in the spring of 2014 to determine criteria and goals for Exploration CO₂ removal systems and gather information on the state-of-the-art of CO₂ removal technologies in the defense, environmental, commercial and academic sectors. The information gathered at these TIMs was used to develop a proposed roadmap, the current version of which is shown in Figure 1. The long-term goal is to develop a technology demonstration, or flight experiment, 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.

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, was 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 current approach and a summary of recent work are presented.

III. Approach

A. Goals and Requirements

The general approach is depicted in the CO₂ Removal Roadmap shown in Figure 1. The blue bar at the top indicates activities on ISS, and includes flight experiments ongoing and planned in the near-term. A description and status of each near-term flight experiment is provided later in this paper. The on-orbit CO₂ removal technology demonstration is shown in the 2020 or 2021 timeframe, depending on the technology readiness level (TRL) of the technologies selected at the end of the 2017 fiscal year (FY17).

Below the blue bar the beige octagons show the development and refinement of requirements used both by the developers to guide their design, and during the gate reviews and down-selection processes. These requirements include interface definitions, acceptable CO₂ levels in the cabin environment, and targeted resource requirements.

B. Technology Development Paths

Next are the “swim lanes” showing the development paths for specific technologies. These will be described individually and in more detail later in this paper. A general description of the two groups follows.

The first five swim lanes show technologies that are on track to reach full-scale TRL 5 technologies by the end of FY17. The green coloring indicates these tasks are fully funded in FY16. The transition to red indicates funding is not fully established for continued development in FY17.

The remaining three green swim lanes that span FY16 only are technologies that are in currently in a conceptual phase (TRL 2 to 3 in general). During the remainder of FY16, material screening and characterization studies will provide data for a gate review at the end of FY16. Two approaches, consisting of a sorbent type and separation process, will be selected for continued development to TRL 4 by the end of FY17.

At the end of FY17, the seven remaining technologies will be evaluated against the criteria established earlier. Additional criteria will be developed as appropriate to rank the technologies. Aside from the standard mass, power, and volume criteria, reliability and safety will also be assessed. Two technologies will be selected for continued development. The two lanes shown to the right of the FY17 downselect represent the maturation path to a flight demonstration system. The upper lane is for technologies starting from TRL 5 (the upper five swim lanes on the far left). The lower lane is for technologies starting from TRL 4 (the lower three swim lanes on the far left). Depending on the results of the downselect, there may be two technologies following the upper path, or two technologies following the lower path, or one technology on each path.

In mid-2019, another downselect occurs. Here, the two remaining technologies are narrowed down to a single final selection for the flight demonstration. Once again the appropriate path depends on the starting TRL level of the chosen technology.
The final swim lane above the “ISS CDRA Reference” section represents technologies, typically at a low TRL level, that are being developed by programs other than ISS or AES and are considered to have high potential and also are high risk. These will also be described later in this paper.

C. ISS CDRA Reference, Objectives, and Figures of Merit

Next, the “ISS CDRA Reference” section provides a top-level understanding of the on-orbit CDRA and crew changes. Two blue swim lanes provide a place-holder for future refinement on the to-be-defined CDRA bed sparing plan and the plan for infusion of Exploration 4BMS technologies to the ISS CDRA.

Finally, the objectives and figures of merit (FOMs) are provided at the bottom of the roadmap. The improvement of reliability to greater than one year between unplanned maintenance events is considered an enabling requirement for an exploration CO₂ system. The second objective shown is to reduce the resource requirements below that of the ISS CDRA for mass, volume, and power; this is considered an enhancing requirement. Finally, an initial performance goal is to maintain the cabin CO₂ partial pressure at or below 2 torr with a crew complement of four. Although this is presently an enhancing requirement, this classification (as well as the CO₂ partial pressure value) is under review due to recent and ongoing studies undertaken to better understand the influence of CO₂ partial pressure on the human physiology.\(^7\,^8\)

### Figure 1. System Maturation Team Roadmap for CO₂ Removal

Green tasks are funded under ISS or AES; red tasks require new funding. Tasks with a gradient in color from green to red are fully funded in FY16 but require additional funding for FY17.

<table>
<thead>
<tr>
<th>Fiscal Year</th>
<th>2016</th>
<th>2017</th>
<th>2018</th>
<th>2019</th>
<th>2020</th>
<th>2021</th>
</tr>
</thead>
<tbody>
<tr>
<td>POA/CM: Jim Knox, Chris Matty</td>
<td></td>
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</tbody>
</table>

- **Objectives/FOMs:** Improved reliability (enabling, >1 year between unplanned maintenance), reduce mass/vol/power (enhancing, <200 kg, 0.4 m\(^3\), 800 W), lower ppCO₂ (enhancing, 4 crew equivalent removal rate at 2 torr cabin ppCO₂)
IV. Status of Roadmap Elements

A. Near-Term Flight Experiments

1. Long Duration Sorbent Testbed

Sorbents that were returned from the ISS CDRA after a year of operation were analyzed to determine (1) the contaminate loading and (2) the resultant loss of working capacity compared with fresh sorbents. Considerable loss of sorbent material working capacity was measured, ranging from 30 to 75% of that for a fresh sorbent. In an attempt to understand the capacity loss, fresh sorbents were doped based on the above analysis and their working capacity evaluated. However, the results showed that the root cause for loss of working capacity is not well understood.

The Long Duration Sorbent Testbed (LDST) as shown in Figure 2 will mimic CDRA operation and expose multiple sorbents of interest for future missions to actual ISS contaminants. It also will expose the current ISS CDRA sorbents in the same manner to provide a control test. A parallel contaminant exposure ground test will be run to determine appropriate flight test durations and viability of ground test analog with limited number of contaminants. The LDST is described in greater detail by Knox and Howard 2016.

![Figure 2. Long Duration Sorbent Testbed flight hardware](image)

B. Technology Development Status

1. Exploration 4-Bed Molecular Sieve (4BMS)

The ongoing and planned tasks for the development of the Exploration 4BMS are shown in

Figure 3. For approximately the first half of FY16, the recently completed 4BMS-X test stand was used in support of ISS CDRA troubleshooting. CDRA desiccant beds were suspected of performing poorly due to downstream evidence of water, and were tested both on with the flight-like ground test CDRA, for system-level testing, and in an extended breakthrough test in the 4BMS-X test stand. The CDRA testing showed essentially the same behavior as ground test beds, and is further documented in Warren et al, 2016.

4BMS Reconfiguration and Testing

Tasks following ISS CDRA support task are shown in

Figure 3, and in FY16 include 4BMS level baseline testing of the new test stand and testing to evaluate the potential of reducing the quantity of desiccant for exploration missions. As described in Table 1, a series of hardware reconfigurations are planned in FY17.
Table 1. Exploration 4BMS reconfiguration rationale

<table>
<thead>
<tr>
<th>Exploration 4BMS Reconfiguration</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual desiccant reduction and CO₂ sorbent bed heater temperature reductions</td>
<td>Depending on CO₂ concentration requirements, the desiccant beds may be oversized. In addition to mass and volume reductions, reduced residual desiccant can allow reduced CO₂ sorbent bed heater temperatures. High sorbent temperatures are linked to accelerated dusting.</td>
</tr>
<tr>
<td>Alternative high-speed blower</td>
<td>The current CDRA blower is limited to approximately 26 SCFM. An alternate blower with a similar form factor has been identified with considerably higher flow range and potentially less sensitivity to overspeed events. This blower will be tested for performance and durability.</td>
</tr>
<tr>
<td>Cylindrical sorbent beds</td>
<td>The CDRA beds have a square cross-section to maximize sorbent volume. As part of the redesign to achieve sorbent containment, some sorbent areas are no longer under spring pressure (used to maintain compaction). Fluidization and accelerated attrition may be the result. Returning to the industry standard of cylindrical sorbent beds insures complete containment and compaction.</td>
</tr>
<tr>
<td>Redesigned heater core</td>
<td>Current CDRA bed heaters have experienced multiple failures, and are designed for beds with a square cross section. The heaters will be redesigned for cylindrical beds. Part of the design process is to evaluate other heater types, such as the spiral-wound cartridge heaters used in the CRCS.</td>
</tr>
<tr>
<td>Modulated repressurization</td>
<td>Repressurization of the CO₂ sorbent beds is currently unmodulated. Standard industrial practice is to control the rate of a fixed bed pressure change to prevent rapid movement and attrition of the sorbent materials due to an inrush of air. The 4BMS will be reconfigured to modulate repressurization to reduce attrition. If the alternate CO₂ sorbent bed is used as the air source, an additional benefit would be the reduction of air-save vacuum pump power.</td>
</tr>
<tr>
<td>CO₂ sorbent bed layering</td>
<td>Zeolites with 2-3 times the CO₂ capacity, and greatly improved kinetics, compared to zeolite 5A have been tested by MSFC recently and have the potential to reduce bed height and increase system efficiency, which becomes more critical with lowered CO₂ levels and higher volumetric flow requirements. However these sorbents will need a protective layer of 5A to prevent water poisoning. Likely failure scenarios must be tested to insure appropriate protection.</td>
</tr>
<tr>
<td>Dust resistant valve</td>
<td>The scope of the current valve redesign was limited due to funding constraints. This effort would extend that redesign to protect all seals from dust intrusion. Local additive manufacturing capabilities would be used to fabricate prototypic valves, followed by bench testing and system testing in the ground test 4BMS systems.</td>
</tr>
</tbody>
</table>
Computer simulation development and simulation studies

Due to the complexity of the sorbent process, with highly nonlinear mass transfer physics that are strongly coupled with heat transfer and momentum transfer physics, mathematical modeling and computer simulations are required to guide many aspects of the design process. For example the selection of sorbent materials cannot be determined by standard figures of merit (FOM), as also demonstrated by researchers working on CO₂ capture from coal-fired energy plants. Here it was found that the standard FOMs could not predict performance in an actual separation process. ¹⁴

Similarly the selection of material type, layer order, layer height, heater temperature set point, cycle times, and flow rates cannot be determined effectively from testing alone. Even if the number of tests required to determine optimal parameters were not prohibitive, testing cannot be used to measure all the internal conditions of the system (such as sorbent loading) thus a great deal of understanding of the system behavior possible with a simulation is lost.

The development of mathematical models and computer simulation of the 4BMS has been an ongoing effort for the last few years, ¹⁵ ¹⁶ culminating in the operational simulation currently being used for the reconfiguration of the Exploration 4BMS system. ¹⁷ As shown in Table 2, comparisons with system operation tests are favorable.

Table 2. CO₂ Removal Rates and Efficiencies ¹⁷

<table>
<thead>
<tr>
<th>HC (min)</th>
<th>Flow rate (SCFM)</th>
<th>Measured Removal Rate (kg/day)</th>
<th>Calculated Removal Rate (kg/day)</th>
<th>Measured Efficiency</th>
<th>Calculated Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>20</td>
<td>3.49</td>
<td>3.41</td>
<td>0.81</td>
<td>0.82</td>
</tr>
<tr>
<td>215</td>
<td>20</td>
<td>3.17</td>
<td>3.12</td>
<td>0.78</td>
<td>0.75</td>
</tr>
<tr>
<td>90</td>
<td>25</td>
<td>4.12</td>
<td>3.73</td>
<td>0.77</td>
<td>0.72</td>
</tr>
<tr>
<td>154</td>
<td>25</td>
<td>4.20</td>
<td>4.30</td>
<td>0.81</td>
<td>0.83</td>
</tr>
<tr>
<td>172</td>
<td>25</td>
<td>4.06</td>
<td>3.90</td>
<td>0.78</td>
<td>0.75</td>
</tr>
<tr>
<td>124</td>
<td>30</td>
<td>5.13</td>
<td>5.18</td>
<td>0.78</td>
<td>0.83</td>
</tr>
<tr>
<td>144</td>
<td>30</td>
<td>4.85</td>
<td>4.62</td>
<td>0.74</td>
<td>0.74</td>
</tr>
<tr>
<td>96</td>
<td>34</td>
<td>5.69</td>
<td>5.82</td>
<td>0.81</td>
<td>0.82</td>
</tr>
<tr>
<td>123</td>
<td>34</td>
<td>5.19</td>
<td>5.44</td>
<td>0.71</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Figure 4. Predicted CO₂ Removal Rate. An illustration of the relative removal rate behavior of the CDRA system in HC/flow rate space. Red dots show calculated points; the surface is interpolated from these.

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An example application is a study on the optimal cycle time and flow rate to maximize the predicted removal rate for the current 4BMS with a 2 torr inlet CO$_2$ condition. The results of this study are shown in Figure 4. From the study, it was found that for the flow rate of 26 SCFM, the maximum CO$_2$ removal rate is achieved at a cycle time of 145 minutes. Detailed information on this study may be found in Coker and Knox 2016.\textsuperscript{17}

**Sorbent screening and characterization**

The final four rows in Figure 3 deal with the screening and characterization of sorbents that are candidates for use in the ISS CDRA and the Exploration 4BMS. In previous development efforts, procedures were developed to expand standard tests for pellet crush strength, bulk crush strength, and attrition.\textsuperscript{2,5} These tests evaluate sorbents after controlled moisture conditioning as well as at the standard dry condition, providing structural strength data for anticipated process conditions.

The characterization and screening of candidate materials is focused on commercially available sorbents but also includes custom sorbents when available. Initial screening with sample quantities of each material involves single-pellet crush testing and pure component CO$_2$ adsorption at multiple temperatures. Further characterization involves pellet and bulk crush tests with moisture conditioning, attrition testing with moisture conditioning, and breakthrough testing and is conducted when more extensive quantities are available.

A subset of the screening results for CO$_2$ sorbents is shown in Figure 5.\textsuperscript{13} Here it is evident that the sorbents with the highest strength do not have the highest capacity, except for the current ISS CDRA sorbent, UOP ASRT, which is no longer produced. These results lead to the release of a request for information (RFI) seeking customized sorbents with the desired properties.\textsuperscript{18} Further information on this work may be found in reference 13.

![Figure 5. Pellet Crush Strength and Capacity for CO$_2$ sorbents. Left: Single pellet mean crush strength, mean crush strength span (error bar), dusting fraction, and dusting initiation force results for 13 CO2 sorbents. Right: Equilibrium CO$_2$ capacity as calculated from Toth isotherms fit to measured pure component CO2 isotherms within a pressure range of 0-20kPa at 25°C. CO$_2$ capacity of ASRT at 2 torr is denoted by a horizontal line for comparison.](image)

Figure 6 shows results from recent sorbent structural characterization testing performed on commercially available sorbents, and two sorbents in use on the ISS CDRA (ASRT 1995 and ASRT 2005), but no longer in production. From these plots, the loss of sorbent strength following moisture conditioning at 0.70 mmHg is evident, although the increase in water vapor pressure to 1.38 mmHg had minimal additional effect on crush strength. For the attrition results, however, the increased vapor pressure did result in significantly increased fines.

Some of the commercial sorbents such as BASF 13X and Grade 544 13X compare reasonably well with the ASRT zeolites across all these tests. However none of the commercial 5A zeolites tested to date have shown good performance for all of these structural tests. Further details on each of these tests may be found in reference 13.

The final lane in the Exploration 4BMS task concerns sorbent contamination. As discussed earlier, sorbent contamination is being examined via the LDST flight experiment, parallel ground testing, and focused studies on the mechanisms of the contamination chemistry, a continuation of studies documented in reference 10.
Figure 6. Pellet Crush, Bulk Crush, and Attrition Test Results for Moisture Conditioned Sorbents. Top left: Pellet crush test results for sorbents at the dry state, and conditioned at 0.70 and 1.38 mmHg water vapor pressure. Top right: Bulk crush test results for sorbents at the dry state, and conditioned at 0.70 and 1.38 mmHg water vapor pressure. Bottom: Attrition test results for sorbents at the dry state, and conditioned at 0.70 and 1.38 mmHg water vapor pressure.

Figure 7. Carbon Dioxide Removal and Compression System
1. Carbon Dioxide Removal and Compression System

The Carbon Dioxide Removal and Compression System (CRCS), shown in 7, is designed to perform both the CO₂ removal and compress CO₂ for further processing. It uses sorbent for both functions, and therefore avoids much of the mass and complexity of a compressor’s rotating machinery. The CRCS design attempts to leverage and synchronize the thermal needs of the removal and compression systems. An integrated CRCS system has been constructed and is being tested. Detailed recent results for CRCS can be found in references 20 and 21.

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.

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 may also be applicable in upgrading 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

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8. James, J. T. "Provisional SMACs for CO₂." Houston, TX, 2013

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