

Prototype Demonstration of the Advanced CO₂ Removal and Reduction System

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ABSTRACT

TDA Research, Inc. (TDA) is developing a simple system that provides an effective way of interfacing the carbon dioxide (CO₂) removal and reduction functions. The system uses a chemical absorbent and a Sabatier catalyst combination to remove the CO₂ and water vapor (H₂O) produced by metabolic processes from cabin air and subsequently reduce the CO₂ to methane and water. The system has the potential to weigh less than the Four Bed Molecular Sieve and CO₂ Reduction Assembly combination, which is connected with a CO₂ pump/compressor and storage tank due to the high CO₂ absorption capacity of the sorbent and its ability to simultaneously absorb both CO₂ and H₂O (which eliminates the need for desiccant beds in the Four Bed Molecular Sieve System). The system does not require a CO₂ pump/compressor or storage tank offering energy savings that come from effective utilization of the heat released by the Sabatier reaction to drive sorbent regeneration. Previously, TDA developed a high capacity regenerable CO₂ and H₂O sorbent to support the operation of the system and showed that the sorbent maintains its activity over extended cycling (Alptekin et al., 2003). We also demonstrated the operation of a state-of-the-art catalyst under the operation conditions of interest (Alptekin et al., 2003). Recently, TDA built a prototype of the system to demonstrate the key aspects of the process. This paper briefly describes the prototype system and summarizes the results of the demonstration tests.

INTRODUCTION

An advanced Environmental Control and Life Support System (ECLSS) for long duration manned space missions –such as planetary flight missions or planetary bases- requires an almost complete closure of all relevant

material loops. Even for low orbit missions, reclamation of oxygen from CO₂ is essential. In the current International Space Station (ISS) operation, CO₂ is vented into space, thus a continuous re-supply of oxygen (in the form of water) to the station is required. In this open loop mode, the launch mass penalty associated with the re-supply is over 900 kg per year when the station has a full crew complement (Jeng et al., 1999) making it necessary to develop new technologies that enable the closure of the oxygen loop. In order to minimize the loss of O₂, the CO₂ removal system must operate in a closed loop mode wherein CO₂ is removed and O₂ is recovered. The air revitalization system (ARS) under consideration contains chains of chemical-physical processes. In these systems, CO₂ is first adsorbed and concentrated over a molecular sieve adsorbent bed, then transferred into a Sabatier reactor by vacuum/thermal desorption and compression which reduces the CO₂ into methane (CH₄) and water. After condensation, water is electrolyzed, producing the needed oxygen and closing the oxygen loop. One of the biggest challenges in closing the oxygen loop is the need to link CO₂ removal and reduction assemblies. The hardware for these two assemblies planned for use on the Space Station cannot be directly connected because the CO₂ removal and the OGA systems have different operation pressures and different operating cycles. The potential solutions for the interface, such as a pump/compressor and a CO₂ storage tank combination, are heavy and large and requires a lot of power to operate.

TDA's Advanced CO₂ Removal and Reduction System (ACRRS) provides an effective interface for the CO₂ removal and CO₂ reduction functions using a chemical sorbent and a catalyst combination to remove CO₂ and H₂O from the cabin air. Subsequently a Sabatier reactor reduces the CO₂ to methane and water. The heat released by the Sabatier reaction is supplied to the sorbent bed

during regeneration to minimize the power requirement. In addition, it reduces the heat rejection requirement for the heat released by the Sabatier reaction.

Description of the System

The ACRRS contains two fixed-bed sorbent reactors, periodically switching positions (Figure 1). In the cyclic process, a slipstream from the crew habitat is directed into one of the sorbent beds with a simple fan. The sorbent absorbs CO₂ and humidity from cabin air, returning air nearly free of CO₂ and humidity back to the cabin. Once the bed is saturated, the gas flow is diverted to a second bed by a series of valves and the saturated bed is regenerated. Before the beds change positions, an air saver pump removes the air trapped in the absorbing bed and pumps it back to the cabin. The air saver pump will reduce the air pressure less than 0.01 psia, which will allow us to operate above the explosive limit of H₂/air mixture. Following air evacuation, regeneration is carried out under hydrogen. Since hydrogen will only be available during the orbital day and its storage is not desirable, the sorbent regeneration is completed during the orbital day. Most of the heat required for the regeneration process is provided by the highly exothermic Sabatier reaction. At the beginning of the regeneration, the hydrogen stream is preheated by resistance heaters to facilitate desorption of CO₂ and H₂O. When the hot hydrogen stream contacts the front end of the bed, the sorbent gives off its CO₂ and H₂O. The hydrogen and CO₂ (driven off of the bed) are sent to a high temperature Sabatier reactor, where they react to produce methane and water. The reactor operates adiabatically, thus the heat released by the Sabatier reaction increase the temperature of the circulating hydrogen. Following the Sabatier reactor, a large fraction of the gas stream is recycled back to the regenerating sorbent bed. Since this gas stream is now hot, the heat input needed by the resistance heaters substantially

decreases. The large recycle stream enables effective transfer of the heat released by the Sabatier reaction into the sorbent bed to drive regeneration. A fan provides the desired gas circulation located at the coldest section in the recycle loop. Approximately, 1/10th of the gas stream from the High Temperature (HT) Sabatier reactor is fed to Low Temperature (LT) Sabatier reactor. This reactor is cooled by the hydrogen feed, transferring part of the heat released by the reaction to the hydrogen. The Sabatier reaction is equilibrium limited, thus, higher conversions can be achieved at lower temperatures. The two-bed design with intercooling ensures high CO₂ conversions. The gas stream from the LT Sabatier reactor, which is now mostly water vapor and methane, is cooled, the steam is condensed and recovered as water, and CH₄ is vented to space. When the regeneration is complete, the bed is evacuated by space vacuum. This removes all the H₂ and methane remaining in the bed, preventing their carry over into the cabin. When it is switched back to the absorption position, the cabin air flow cools the bed, effectively dumping the heat stored in the bed into the cabin air from which it is ultimately rejected to space. The space purge and subsequent reduction of hydrogen pressure will allow us to operate below the explosive limit of H₂/air mixture.

Prototype Development

Previously, we developed a sorbent that can effectively remove CO₂ and H₂O from cabin air and tested its performance under representative conditions for 500 cycles. The sorbent maintained its CO₂ and H₂O absorption capacity for 500 cycles without spalling or undergoing any undesirable side reactions. Next, we developed a Sabatier catalyst that would effectively catalyze the CO₂ reduction in the presence of high concentrations of water vapor (since water is removed from the cabin along with CO₂). Recently, TDA designed and built a prototype unit to demonstrate the concept of

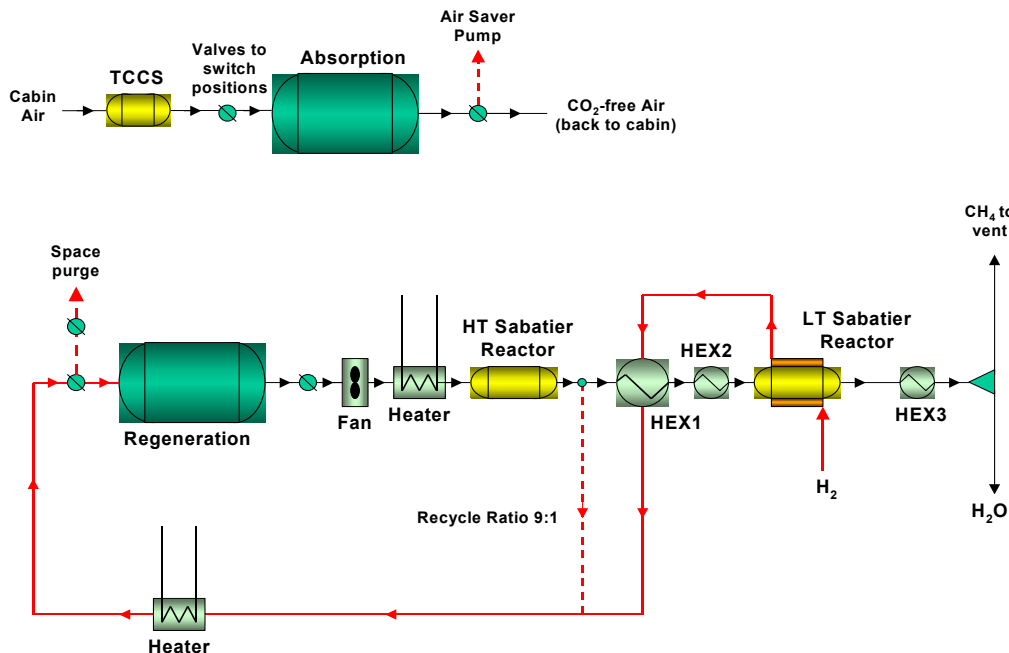


Figure 1. Schematic of TDA's ACRRS.

combined CO₂ and H₂O removal from a simulated cabin air stream and subsequent CO₂ reduction in a single unit. The prototype is sized for a capacity of 4-crew person equivalent. The unit contains one sorbent reactor (which is sequentially operated in the absorption and regeneration modes to simulate the whole cycle), both a high temperature and a low temperature Sabatier reactor (operated adiabatically with external insulation), a high temperature fan to provide gas circulation, vacuum pumps to evacuate the gases in between absorptions and regenerations, control systems and all auxiliary

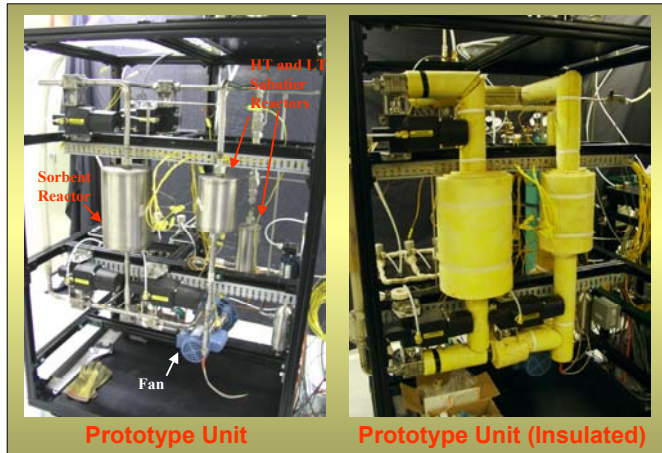


Figure 2. Photograph of ACRRS prototype unit designed for 4 person crew.

components including regulators, valves heaters and transducers to allow the full demonstration of the concept. Figure 2 presents a picture of the hardware fabricated at TDA and delivered to NASA Johnson Space Center for further evaluations. Due to time and budget constraints, the system is built by using commercial parts for demonstration purposes only to show the key aspects of its operation. It is not flight rated or qualified for human testing. The packaging of the components does not reflect the most compact design (an inherent weight penalty exists as a result of using commercial components). However, despite the simplifications, the prototype unit

provides an excellent basis for demonstrating the concept, including the operation of the sorbent and the catalyst under simulated operation conditions, and the effectiveness of the heat integration between the Sabatier reactor and the sorbent bed in regeneration.

Figure 3 shows the flow path during the absorption and regeneration steps. The absorption performance of the sorbent is tested using flow path A. The air enters in and flows through the bed at low temperature where CO₂ and H₂O are removed by the sorbent. Following absorption, the first step of regeneration is to isolate the sorbent bed and evacuate it to prevent the formation of a combustible hydrogen/air mixture since hydrogen is employed in bed regeneration. After evacuation, the system valves are configured to create a re-circulating flow path that includes the sorbent bed (Bed 1), the recirculation blower, the high temperature Sabatier reactor (Bed 2), and the recirculation gas heater. The gas then flows back out through the air saver pump, which can be activated at the end of the adsorption to purge the bed. During the regeneration cycle, hydrogen is introduced into the system through path B. It flows through the center of the Low Temperature Sabatier reactor through an external heat exchanger, not mixing with the gases reacting in the Sabatier reactor. Path C indicates the recycle flow impelled through the loop by a fan. The high gas temperature causes the CO₂ to desorb from the sorbent. The gas flows around the loop continuously. 1/10th of this flow is continuously removed through path D. At several locations in the prototype, CO₂ and H₂O levels will be measured.

Sorbent Reactor: The largest component in the system is the canister that houses the sorbent. The weight of the sorbent and the volume of the sorbent canister were estimated based on the experimental data. With the known amount of CO₂ removal rate and absorption duration, we calculated the amount of CO₂ absorbed in one cycle. Using the sorbent capacity, we estimated how much sorbent was needed, and from the sorbent density how much reactor volume was required. The design space velocities are 4,000 h⁻¹ and 800 h⁻¹ for the

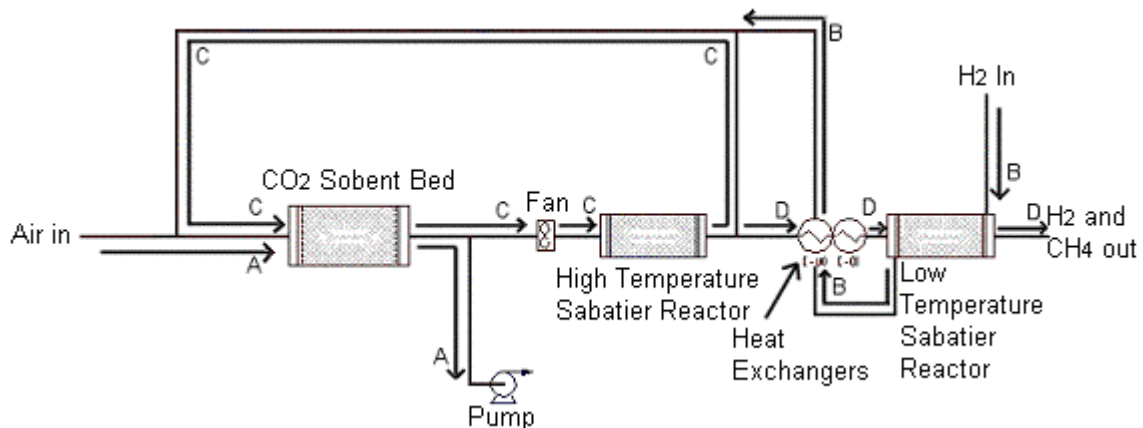


Figure 3. The schematic of the flow paths for the ACRRS prototype unit during absorption and regeneration. Path A indicates the flow of air through the sorbent bed during the adsorption step. Path B is the flow of hydrogen through the heat exchangers into the regeneration loop. Path C designates the flow around the regeneration loop. Path D is the path from the regeneration loop through the low temperature Sabatier reactor.

absorption and regeneration, respectively. The bed designed for CO₂ removal is also capable of actively controlling cabin air humidity level.

In order to provide flexibility to the reactor orientation and prevent the gas channeling the sorbent pellets, in the actual system a spring-loading mechanism holds the sorbent pellets in a tightly packed configuration (the sorbent reactor uses a fixed screen at one end and a removable screen in the other end, which is compressed by a spring to keep the sorbents tightly packed). However, for simplicity, we selected a vertical configuration for the prototype reactor, which did not require the spring loading.

The sorbent reactor is oversized with the capability of housing up to 7.285 L of sorbent pellets. We loaded only 3.1 kg (4.2 L) of sorbent pellets. We oversized the reactor

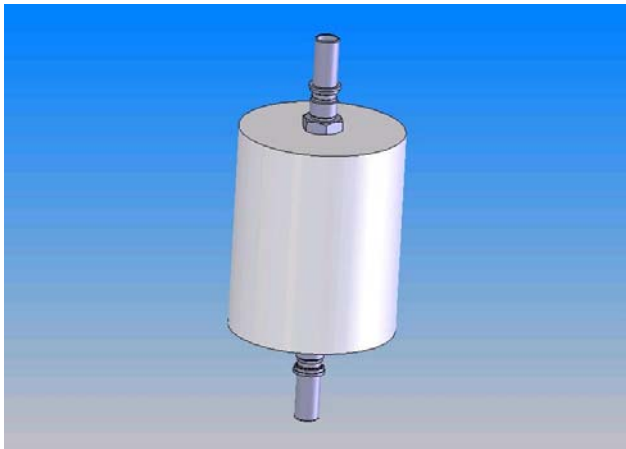


Figure 4. Drawing of the sorbent reactor.

to allow changing operating conditions and system rating as necessary using the same setup (e.g., if more sorbent is needed). The reactor is made of SS 304 vacuum tubing with 8" in diameter and 11.4" long (a cylindrical vessel with an aspect ratio of 1.4) as shown in Figure 4. The wall thickness was 0.125", providing roughly 7.76" internal diameter. Relatively thick walls are required to be able to hold vacuum (during the evacuation steps, the system pressure goes below 0.1 psia). The reactor is externally insulated using 2.0" insulation material to prevent heat losses during regeneration.

High Temperature and Low Temperature Sabatier Reactors: The design of the adiabatic high temperature Sabatier reactor was straightforward. Figure 5 shows the dimensions of the reactor vessel. We used 6" diameter 0.083" wall 304LSS vacuum tubing for the reactor body and welded 6" diameter 0.090" plate ends to make the reactor. The Sabatier reactor is also oversized, we loaded only 1.56 kg (2.4 L) of catalyst pellets in the form of 1/8" diameter cylindrical pellets. The reactor is insulated using 2.0" insulation material to prevent heat losses during regeneration.

For the low temperature Sabatier reactor, we used a similar design that resulted in a 4" diameter 7.88" tall cylindrical reactor (0.083" wall 304LSS vacuum tubing for the reactor body and welded 4" diameter 0.090" plate ends). The low temperature Sabatier reactor contains

0.68 kg (1.1 L) of catalyst pellets in the form of 1/8" in diameter cylindrical pellets. The reactor is insulated using 2.0" insulation material to prevent heat losses. In the real system, the low temperature Sabatier reactor is hydrogen cooled to maximize the amount of heat recovered. TDA's low temperature Sabatier design was taken from Strumpf, Chin, Lester, and Homeyer, (1991) "Sabatier Carbon Dioxide Reduction System for Long-Duration Manned Space Application," SAE paper 911541 (we simply replaced the air flow with hydrogen). We used a simpler design in the prototype.

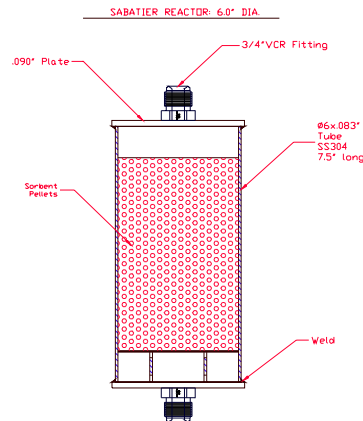


Figure 5. Schematic of the High Temperature Sabatier reactor.

Gas Re-circulation: For gas circulation in the loop, we used an off-the-shelf blower rated for combustible gases that can tolerate temperatures up to 180°C. We carefully monitored the progress of the heat wave in the regenerating sorbent bed because the temperature rating of the blower is lower than desired regeneration temperature. Calorimetry was performed on the desorption heater to estimate the flow recirculation rate since the high temperature, variable composition and very low pressure drop requirement obviates the use of most gas flow meters in this system.

Diagnostic Tests

First, preliminary tests were performed to elucidate the operational characteristics of the CO₂ sorbent bed and the associated hardware using simulated cabin air for absorption and nitrogen for regeneration. During these initial tests, the Sabatier reactors were empty with the attention focused on testing the performance of the sorbent. Because CO₂ was not removed by reaction with H₂, but was instead recycled back to the sorbent bed, desorption and subsequent removal of all the CO₂ took longer than expected in comparison to the actual operation. The water desorbed from the sorbent was also re-circulated back through the sorbent bed but in this case its concentration was lower due to the lack of generation of H₂O in the Sabatier reactor. These tests were therefore informative, but not quantitative with respect to the performance one can expect from the full system.

As part of the initial tests, we carried out a total of 7 cycles where we measured the CO₂ and H₂O capacity of the

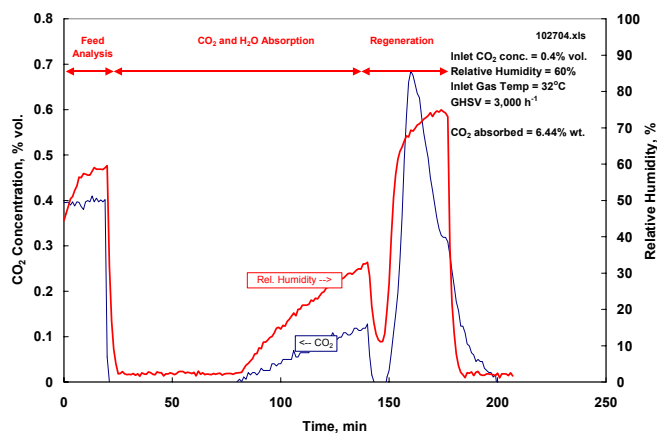


Figure 6. Typical CO₂ absorption profile in the prototype unit during the initial tests, GHSV= 3,000 h⁻¹ for absorption and regeneration (gas flow was 4 times higher than designed for the regeneration).

sorbent and optimized system operation. The CO₂ and H₂O inlet partial pressures were 3.1 and 12.0 torr, respectively and the air flow was 11.5 cfm (327 slm). Figure 6 shows the typical CO₂ absorption profile in the prototype unit during the initial tests. The sorbent achieved a CO₂ capacity around 5.6 to 7.0 % wt. through 7 cycles. We observed that the absorption capacity strongly depends on the moisture content of the feed gas with higher absorption capacity achieved at higher H₂O partial pressures. During these initial tests, we looked at the impact of operating parameters such as the inlet temperature. As indicated in Figure 7, the sorbent performed better at the lower gas inlet temperatures; the absorption capacity at 23°C was 0.55% wt. higher in comparison to that can be achieved at 32°C under identical conditions.

Demonstration Tests

After carrying out the diagnostic tests at various operation conditions (i.e., temperature, inlet and outlet gas concentrations) to verify the performance of the individual components of the prototype unit, the key aspects of the concept were demonstrated, including the operation of the

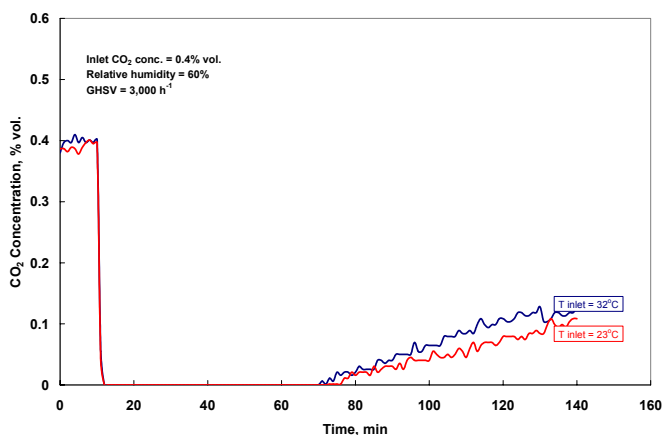


Figure 7. Effect of temperature on the CO₂ breakthrough profile. GHSV= 4,000 h⁻¹.

sorbent and its efficacy for combined CO₂ and H₂O removal, its integrated operation with the Sabatier catalyst, and the effectiveness of the heat integration between the Sabatier reactor and the sorbent bed.

During these tests, the sorbent bed treated a simulated cabin air flow of 11.5 cfm (327 slm) and removed CO₂ and H₂O for 120 minutes. Figure 8 shows the gas flows during absorption and regeneration in a typical demonstration test. At the end of the 120-minute absorption, a vacuum pump removed the air from the reactor dead space and reduced the pressure of the sorbent bed to less than 0.1 psia simulating the operation of an air saver pump. The evacuation took place in less than 3 minutes. The sorbent regeneration was carried out in a flow of hydrogen. We varied the H₂:CO₂ molar ratio from 2.6 to 4.0 in a series of tests (the former representing the conditions at International Space Station, the latter the stoichiometric requirement). The sorbent regeneration was completed in 120 minutes. Following the regeneration, the system is evacuated again for 3 minutes, and cooled with the flow of cabin air to the absorption temperatures in less than 10 minutes. The second evacuation prevented the contact of hydrogen remaining in the reactor dead space with the oxygen (or any hydrogen leakage into the cabin).

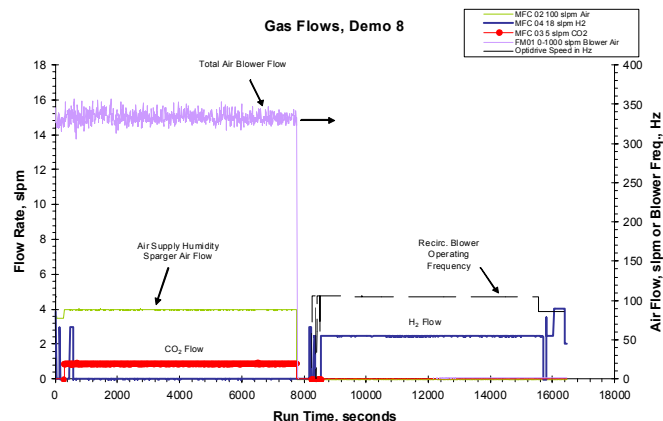


Figure 8. Gas flows during absorption and regeneration during the Demonstration Test #8.

Hydrogen was introduced to the loop at various flow rates from its high-pressure storage bottle using an electronic mass flow controller to adjust the overall H₂/CO₂ molar ratio. Hydrogen was mixed with the re-circulating flow, which was then heated to approximately 400°C before entering the top of the sorbent bed. We selected a higher temperature set point for the regeneration in order to complete the sorbent regeneration in a short time (although such high temperatures are not needed for the CO₂ desorption, high regeneration temperatures increases the rate of the decomposition). The recirculation flow rate in the loop was selected to be nominally 1/4 of the absorption air flow rate (i.e. 324/4 = 81 slpm), although this was increased in later runs to help speed up the desorption process. The flow rate in the circulation loop was adjusted with a blower connected to a frequency control device that controls the frequency of the pump and thus the gas flow and discharge pressure.

Figure 9 shows the temperature profiles of various points within, on, and upstream of the sorbent bed during the absorption and regeneration steps. Regeneration was initiated by running a hot hydrogen flow of 8 slpm into the sorbent bed. During regeneration the flow is directed from the top of the bed downward to insure both internal hydrodynamic stability as well as to minimize the time required for regeneration by avoiding having to push

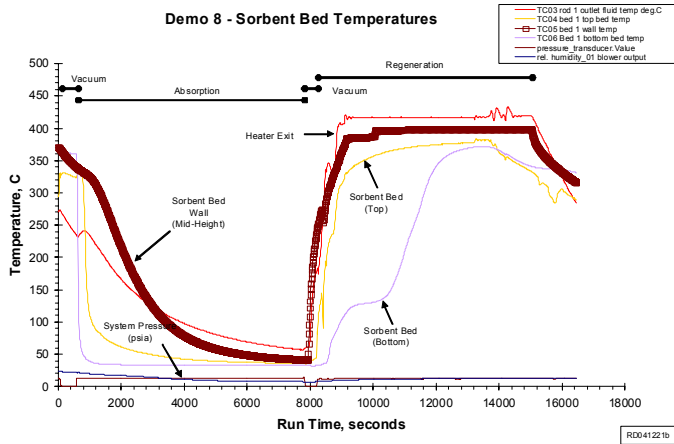


Figure 9. The sorbent bed temperatures during absorption and regeneration during Demonstration Test #8.

absorbed CO₂ and water completely through the bed. The top sorbent bed thermocouple responded rapidly to heating of the incoming gas stream but had an offset due to system heat losses between the heater exit and the top of the sorbent bed. The thermocouple located near the bottom of the sorbent bed warmed and plateaued initially due to reaction of the CO₂ and water in the re-circulating gas flow, then warmed significantly as the thermal wave associated with the regeneration process reached the bottom of the bed.

Figure 11 presents the concentration profile of the gases exiting the system during regeneration on a dry basis at a H₂:CO₂ molar ratio of 2.6. As expected, at the beginning of the regeneration a large fraction of the hydrogen exited the system unreacted since no CO₂ were released due to the low temperature of the sorbent bed. As the bed warmed up, CO₂ and water was released and CO₂ reacted with H₂ to produce CH₄ and more water. When the CO₂ released from the bed reached to its maximum, more than 60% (± 15%) of the hydrogen fed to the system was utilized in the Sabatier reaction. We also estimated that 64% (± 15%) of the CO₂ was converted into methane (high uncertainty is due to the difficulties in measuring the exit gas flow from the system).

We carried out consecutive absorption/regeneration cycles to evaluate the performance of the prototype unit. The unit achieved all performance goals other than the regeneration of the sorbent within the planned duration. Due to the availability of hydrogen during the orbital day, in our system design, we aimed regenerations to be completed in less than 53 minutes (within the orbital day). However, it took 120 minutes to drive off the CO₂ and water vapor from the bed and regenerate the sorbent. Although in our bench-scale tests, we showed that the sorbent regeneration could be completed in 50 minutes, the high mass of the prototype sorbent reactors, large heat losses from the unit (which is specifically designed for the demonstration purposes) and the limitations with the heaters and the fan used in the system reduced the effectiveness of the heat supply to the sorbent pellets and increased the regeneration time.

Stability of the Sorbent

During the demonstration tests, we observed an average

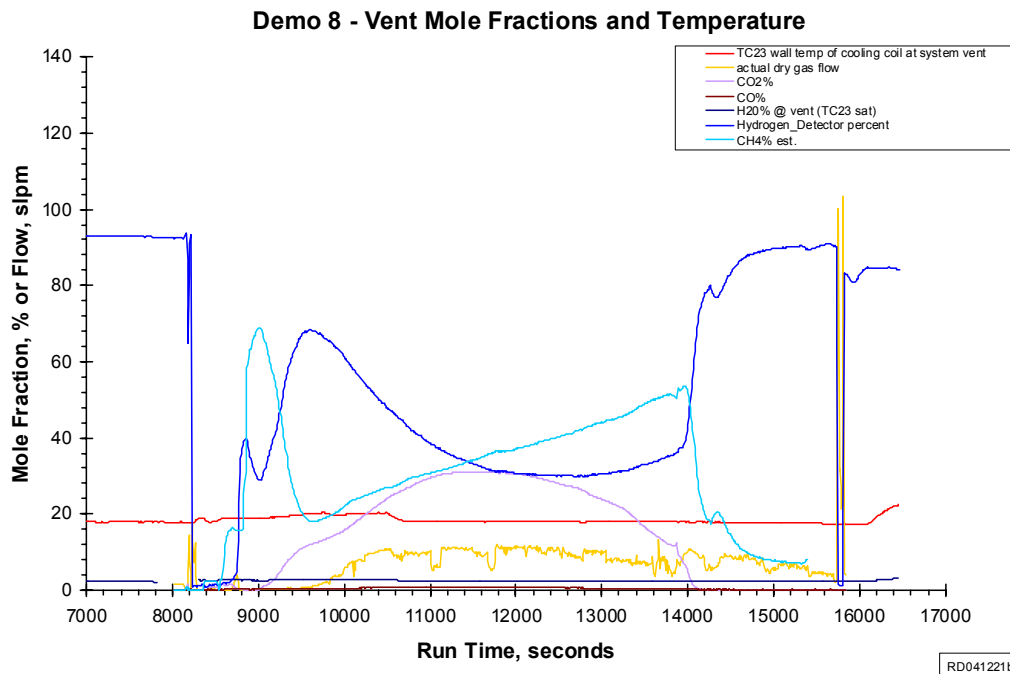


Figure 10. Vent mole fractions during the regeneration step of Demonstration Test #8.

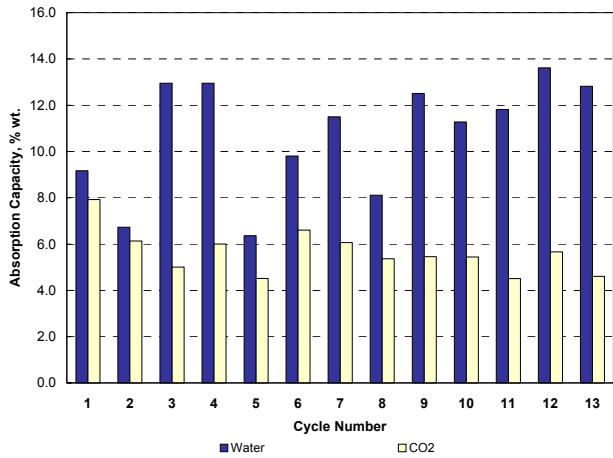


Figure 11. CO₂ and H₂O absorption capacity of the sorbent during prototype demonstration tests.

absorption capacity of 5.6 and 10.7 wt for CO₂ and H₂O, respectively (Figure 11). Some of the large variations in the absorption capacity of the sorbent were due to the drastic changes in the test conditions, in an effort to identify the optimum conditions of the prototype unit and to identify the limits for its operation. The measured capacities for the sorbent during the demonstration tests are in good agreement with our prior bench-scale measurements.

One of the ways to ensure the stability of the sorbent was to monitor the pressure drop across the sorbent bed through the cycles. One should expect an increase in the bed pressure if the sorbent pellets breakdown and form dust in the bed. Figure 12 shows the pressure of the sorbent bed at various cycles. We observed that the pressure of the bed was stabilized after an initial increase. This indicates that the sorbent pellets maintained their mechanical integrity throughout the initial testing.

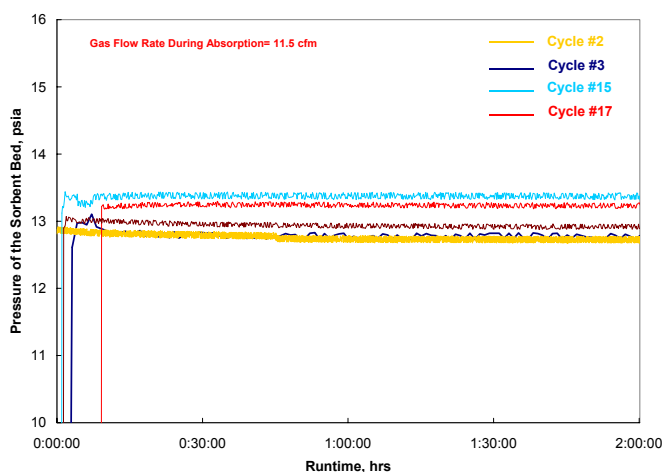


Figure 12. Pressure of the sorbent in different cycles (absorption step only).

System Analysis

After demonstrating the technical feasibility of the concept, we carried out a preliminary system analysis based upon

major system components. We used the experimental data in the design of the sorbent beds and the Sabatier reactors. We carried out mass and energy balances across each unit to calculate the temperature, pressure, flow rate and composition of each stream in the CO₂ removal/reduction system. We then sized the units based upon the performance criteria. The system analysis suggests that ACRRS weighs about 107.6 kg, representing a 191.4 kg reduction compared to the potential 4BMS+CRA combination. If the weight impact associated with the power generation and heat rejection is taken into consideration, the weight equivalency of TDA's ACRRS is 457.5 kg less than that of the Four Bed Molecular Sieve and CO₂ Reduction Assembly combination (a 31% reduction). The details of the analysis are reported elsewhere (Alptekin et al., 2005).

CONCLUSIONS

In the prototype system, we first showed the effectiveness of the sorbent under nominal spacecraft conditions. The sorbent treated a 25 cfm of simulated cabin air flow (T= 25°C, 4kPa CO₂, 50% relative humidity) and controlled both the CO₂ and H₂O concentrations at the desired levels, achieving average absorption capacities of 5.64% and 10.7% on a weight basis, respectively. In the prototype unit, we showed that sorbent can be regenerated at modest temperatures under a flow of hydrogen and the released CO₂ can be converted into methane and water using a series of Sabatier reactors. In the demonstration tests, we also showed that the heat generated by the exothermic Sabatier reaction can be effectively utilized in regenerating the sorbent with the use of a gas recycle. Altogether, we ran 13 complete absorption/regeneration cycles in the prototype. The unit will be delivered to NASA for further testing and evaluations. The preliminary system analysis results carried out on all major components used in the system (e.g., sorbent reactors, Sabatier reactors) suggest that TDA's CO₂ removal/reduction system weighs 107.6 kg, 191.4 kg less than the current candidate system (4BMS and Sabatier assemblies interfaced with a CO₂ pump compressor and storage tank); this is a 64% reduction in initial launch weight (on a preliminary basis).

Overall the demonstration in the prototype unit was successful. We showed that the combined removal of CO₂ and H₂O and subsequent reduction of CO₂ in a single unit under representative operating conditions. Both the sorbent and the catalysts met the performance goals. Engineering improvements and intelligent design of the sorbent reactor has the potential to further improve the results. The prototype unit is delivered to NASA for further testing and evaluations.

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