Innovative Method for CO2 and H_2O Sequestration and Reclamation in Long Duration Exploration Portable Life Support Systems (xPLSS)

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The National Aeronautics and Space Administration (NASA) has a clear need to develop new technology to meet the challenging objectives of long- term space missions included in the Artemis Program. New objectives include sending astronauts to the surface of the Moon and then embarking on missions to Mars. Many of the missions exploring the lunar surface and Martian environment will be longer than current extravehicular activity (EVA) time frames and therefore the development of new, robust, and lightweight life support systems will be required. In these EVA applications, the control as well as conservation of CO2 and H_2O is critical. Historically, the Metox has been used to remove CO2 from the Extravehicular Mobility Unit (EMU) during EVA's. However, this unit utilizes a solid silver oxide sorbent which requires a high mass and volume allocation and requires regeneration in between missions at a temperature of 205°C. The technology currently planned to replace the Metox in the Exploration Extravehicular Mobility Unit (xEMU) is the Rapid Cycle Amine (RCA). This device utilizes a regenerable, pressure swing adsorption system which adsorbs CO2 and H_2O from the suit and then desorbs said compounds through exposure to space vacuum. While this device does not have a finite capacity like the Metox, the desorption of the H_2O and CO2 to vacuum prevents the reclamation of these compounds which may be unacceptable in advanced EVA environments where resources are limited.

In this SBIR Phase I project, Reaction Systems developed a novel system which utilizes a high-capacity liquid sorbent and a hollow fiber module to control CO_2 and H_2O under EVA conditions and allows for the reclamation of both removed products. The system was challenged with an inlet CO_2 flow rate representative of a metabolic rate of 2000 Btu / hr and residence time representative of full scale conditions. It maintained the outlet CO_2 concentration at a constant value of 0.05%, or 0.31 mm Hg, which is significantly lower than the required level of 3.0 mm Hg. In addition, the system was able to maintain the outlet humidity content of the process stream at 40% relative humidity (RH) when challenged with inlet humidity ranging from 40%-90% RH.

Nomenclature

Acfm = actual cubic feet per minute
°C = degrees Celsius
°F = degrees Fahrenheit
Btu/h = British thermal units per hour
CO_2 = carbon dioxide
EMU = Extravehicular Mobility Unit
EVA = extra vehicular activity

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ft^3 = cubic feet
g/h = grams per hour
h = hour
HFM = hollow fiber module
H_2O = water
in = inch
L = liter
mg = milligram
mm = millimeters
mm Hg = millimeters of mercury
NASA = National Aeronautics and Space Administration
N_2 = nitrogen
OD = outer diameter
PLSS = Portable Life Support System
$ppCO_2$ = partial pressure of CO_2
psia = pounds per square inch absolute
RCA = Rapid Cycle Amine
RH = relative humidity
s = second
SBIR = Small Business Innovative Research
sccm = standard cubic centimeters per minute
slpm = standard liters per minute
wt% = weight percent
xEMU = Exploration Extravehicular Mobility Unit

I. Introduction

The challenges associated with long term space missions such as those associated with the Artemis Program require the development of new and innovative technologies. Challenging new objectives include sending astronauts to the surface of the Moon and then embarking on missions to Mars (NASA 2024)[1]. A critical aspect of these long-term missions is the ability to recover and recycle valuable resources such as CO_2 and H_2O. In addition, many of these missions will involve longer EVA times and therefore the development of new, robust, and lightweight life support systems is required. The Exploration Extravehicular Mobility Unit (xEMU) has been identified as the suit that will be tested on the Gateway stack to demonstrate its capability for EVA. After that it would be used on Mars transit missions, and with small upgrades, the suit could be used on the surface of the Moon. Moreover, the xEMU is intended for use in the Martian environment and it is designed to last up to 500 days on the surface. In all of these EVA applications, it is critical to recover CO_2 and humidity and to maintain each at safe levels in a compact and effective configuration for the duration of the mission.

Sizing the suit components requires that estimates of CO_2 and H_2O generated be made. Over the course of an EVA, the rate of CO_2 produced depends on the average metabolic rate of the crewmember. Typical CO_2 production rates range from 0.49 g/min at a metabolic rate of 350 Btu/h up to 3.2 g/min at a metabolic rate of 2000 Btu/lb [2]. Therefore, the system needs to be sized to handle at least the average production rate for the duration of the EVA, while maintaining the maximum CO_2 partial pressure (PP_{CO2}) at its outlet at 3.0 mm Hg. Historically the METOX system has been used to control CO_2 control in EVA. This unit contains a silver oxide sorbent that reacts with CO_2 to form silver carbonate. Auman et al [3] list six individual reactions involved with this process which involve H_2O, Ag_2O and CO_2, however the series results in the overall reaction shown below:

$$Ag_2O + CO_2 \rightarrow Ag_2CO_3 \tag{Rxn 1}$$

Ag_2O and CO_2 have molecular weights of 231.8 g and 44 g, respectively, and therefore the Ag_2O sorbent to CO_2 weight ratio is 5.3 to 1. Therefore, for every gram of CO_2 that is removed from the spacesuit, 5.3 g of silver oxide sorbent is required. Auman et al. [3] carried out a deactivation study on the METOX and estimated that the average metabolic rate over an entire EVA is 850 Btu/h. At this rate, the CO_2 generation rate is 0.17 pounds per hour (1.39 g/min) and a total quantity of 650 grams of CO_2 would be produced over an 8.5-hour EVA. Thus, a total of 3.47 kg of Ag_2O would be required to meet that demand, assuming 100% adsorption efficiency. After conversion to Ag_2CO_3

the total weight is 4.13 kg, resulting in a CO_2 loading of 16 wt%. After the sorbent had been consumed, it must be regenerated by heating it to 205°C before it can be reused [3].

Auman et al. [3] report that the sorbent in the METOX is coated on 90 rectangular plates that are 0.083 inches (2.1 mm) thick. The plates are wrapped in polytetrafluoroethylene (PTFE) and are enclosed by perforated stainless steel sheets. While the sorbent has worked well, increasing the size of the METOX to handle the longer duration EVA presents several challenges. First, there is always the tradeoff between the thickness of the layer and effective use of all of the material. Increasing layer thickness increases capacity up to a point, but past that, the interior layers of sorbent are not used as effectively. In addition, if the sorbent becomes deactivated or it spalls off the sheet, a major overhaul of the unit is required.

Further, recent reports show that there have been instances where a loss of performance was observed with the original design of the METOX [3]. These efforts note that in several EVAs, CO_2 breakthrough occurred sooner than was expected, based on the calculated METOX capacity and the crew member's metabolic rate. The results of a subsequent investigation indicated that performance could have been impacted by alkali salt migration from the inlet side of the sorbent sheet to the outlet side. In addition, the investigation found that the effects were more noticeable at the surface of the sorbent compared to the core[3].

Although new technology is being developed to replace the METOX, it was not designed to accommodate the new, long-duration missions. The Rapid Cycle Amine (RCA) uses two separate beds that alternate between being on-line to remove CO_2 and H_2O and being off-line for regeneration. Unfortunately, regeneration is accomplished by exposing the bed to space vacuum, which results in the loss of all of the CO_2 and moisture that had been absorbed on the bed. Additionally, the RCA is incapable of operation on Mars as a result of the density and high concentration of of CO_2 in its atmosphere. Clearly a more effective method to control and collect CO_2 and RH is required for future exploration missions. In addition to retaining these compounds, the new method should have a lower weight ratio of sorbent to CO_2, be regenerable at a lower temperature than 205°C, exist in a form that maintains performance when a portion of the sorbent becomes contaminated, and can be replaced easily if it loses capacity.

A. Improved Method for CO_2 and Moisture Control

A potentially better approach for this application is the use of a liquid sorbent that can contain the CO_2 and H_2O produced in an EVA. Since the sorbent will not be exposed to space vacuum during the EVA, sorbents with relatively low boiling points can be considered. The use of a liquid sorbent combined with a high-efficiency contactor eliminates the problems associated with solid sorbents attached to a sheet metal surface. For example, the entire quantity of a liquid sorbent can be loaded with CO_2 as opposed to only the most available surface layers of a solid sorbent. In addition, the use of a liquid sorbent eliminates the dangers of a surface contaminant affecting the performance of the entire sorbent inventory. Moreover, if the unit begins to show a decrease in performance, a liquid sorbent can be drained and replaced. Finally, liquid sorbents have the potential to be regenerated after each mission at lower temperatures than those required for the METOX. Additionally, they can also absorb H_2O.

The objective of this Phase I project was to develop a new system that utilizes a high efficiency contactor and a liquid sorbent system to control CO_2 and H_2O. The improved system will maintain the partial pressure of CO_2 at its outlet at 3.0 mm Hg or less, retain the CO_2 and moisture removed from the ventilation loop, and be fully regenerable with moderate heat once the liquid sorbent reaches capacity. In the following sections, the approach Reaction Systems employed to achieve this objective is described.

1. Strategy for Developing New Sorbents

A schematic of Reaction Systems' approach used in this project is shown Figure 1. The system consists of a hollow fiber membrane module and an inventory of liquid sorbent. Hollow fiber modules (HFM) provide the highest surface area to volume ratios of any membrane system [4]. In a gas scrubbing application, it is recommended that the gas phase flows through the lumen side of the module (through the inside of the hollow fibers) while the liquid flows through the shell side in a countercurrent configuration. The schematic shows that the gas and liquid flows are oriented in this fashion and that the liquid sorbent is circulated by a dedicated pump.

The successful application of such a system depends on the performance of a number of metrics including the rate at which CO_2 and moisture are removed from the gas flow, the capacity of the liquid sorbent, and the regeneration conditions required to recover any CO_2 and H_2O that are absorbed. The rate at which CO_2 is removed from the gas stream is of particular importance and will be determined by the differential CO_2 partial pressure between the gas flow and the liquid sorbent. The CO_2 partial pressure in the liquid sorbent will need to be sufficiently low relative to the gas stream partial pressure in order to maintain a high enough driving force for adsorption by the liquid sorbent. As will be discussed later in this report, these issues were addressed in the Phase I project and the results clearly show that this system has excellent promise for use in this application.

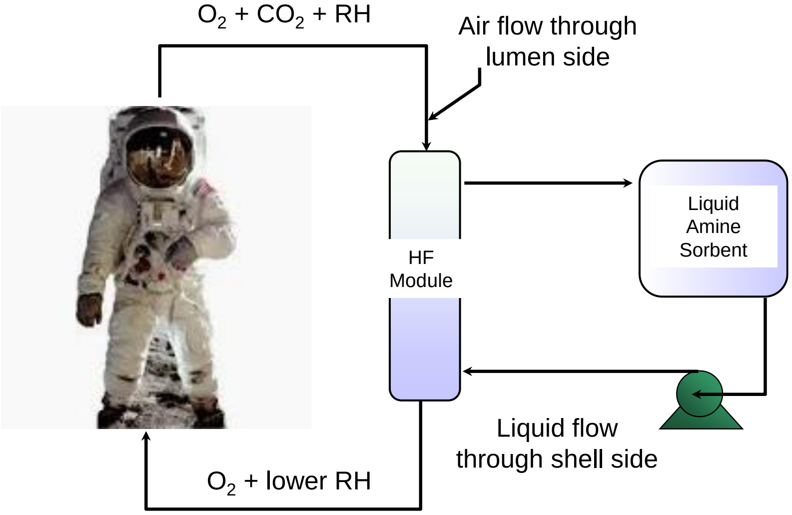


Figure 1. Schematic of a CO_2 control system using a liquid sorbent and high efficiency contactor.

2. *High Efficiency Contactor*

Initial calculations were carried out to identify the removal rates that were needed to meet the demands of these long duration missions. The module must be large enough to allow the required CO_2 to permeate through the fiber walls without exceeding the allowable pressure drop of 2 in. H_2O. In addition, the module must be able to remove up to 3.2 g CO_2 per minute (2000 Btu/h) while maintaining the outlet partial pressure at a maximum of 3.0 mm Hg. Moreover, the sorbent inventory must have the capacity to contain at least the 650 g of CO_2 produced during an 8.5 hour EVA and potentially more with the anticipated extended EVA times [2]. As specified in the Phase I solicitation, the total volume of the system should be no greater than 0.231 ft^3. The two primary components of the proposed system are the contactor and the sorbent inventory. Therefore, the size of the contactor depends on the sorbent loading.

II. Experimental Procedures

In this section, the experimental procedures used in this Phase I project are described. In Section A the rationale for selection of some of the sorbent materials is also included. Section B includes a description of the system used to characterize the sorbent mixture performance and the procedure used to carry out these measurements.

A. Preparation of Candidate Sorbent Materials

A critical parameter in the design of a full-scale system is the capacity of the liquid sorbent for CO_2 because it directly affects the quantity of sorbent that must be contained in the system and also sets the size of the liquid contactor. As mentioned previously, the total quantity of CO_2 produced in an EVA is 653 g, and therefore the quantity or inventory of liquid sorbent can be estimated based on its CO_2 capacity. For example, a loading of 15.9 wt% would result in the same weight of sorbent as needed for the silver oxide sorbent in the METOX, 3.46 kg not including the weight of the plates used to support the sorbent. On the other hand, if higher loadings could be obtained, for example 20%, that would reduce the amount to 2.62 kg, a reduction of 0.84 kg. Assuming a density of about 1 g/cc, the volume of sorbent required would be 0.093 ft^3 or 2,633 cm^3.

In a recently completed Phase I and an ongoing Phase II Small Business Innovative Research (SBIR) project, Reaction Systems is developing CO_2 sorbents for use in the RCA [5]. In this application, a high CO_2 cyclic capacity is required under pressure swing conditions. However, in the application in this project, the sorbent can be regenerated at the conclusion of the EVA, and therefore thermal regeneration can be employed, which typically produces higher cyclic CO_2 capacities. The RCA sorbents are high molecular weight, amine-based liquids that are impregnated on high surface area polymethylmethacrylate (PMMA) beads. However, some of the liquids have a sufficiently low enough viscosity that they could be circulated on the shell side of the module in excellent contact with the process flow on the lumen side of the module. In addition, these compounds have high densities which reduce volume.

In this project the amine sorbents were combined with H_2O in a reservoir at concentrations ranging from 90% sorbent/10% H_2O to 50% sorbent/50% H_2O. In an actual PLSS application, the H_2O would be contained with liquid sorbent and not require additional volume allocation. Benefits of H_2O include reducing the viscosity of higher molecular weight amine compounds and also dissolving amines that are solids at room temperature.

An additional benefit from H_2O is that it has some capacity for CO_2. Removing CO_2 from gas streams is an area of current interest and several recent efforts have measured CO_2 permeation rates though hollow fiber module with an aqueous based liquid flowing on the shell side. Jeong et al.[6] flowed 43.6 vol% CO_2 through a LIQUI-CEL hollow fiber module at a rate of five liters per minute at a total pressure of 5 atm. The module had a diameter of 2.5 inches (6.35 cm) and a length of 8 inches (20.32 cm), and its reported surface area was 1.4 m^2. The authors obtained 97% removal of the CO_2 using a H_2O flow of three liters per minute on the shell side of the module. These measurements are equivalent to a removal rate of 0.43 moles CO_2/min with an average pressure differential of 1.12 atm, and therefore the permeance is 0.28 mole CO_2 /(min m^2 atm). This rate is within a factor of five of that derived earlier with a module volume of 0.05 ft^3 or 1,416 cm^3.

Other modifications can be made to the aqueous phase that could increase the absorption rate. The reactions required for CO_2 to absorb in H_2O are shown below:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad \text{Rxn 2}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad \text{Rxn 3}$$

Therefore, absorbing CO_2 in H_2O educes the pH, which can reduce the subsequent reaction rate of additional CO_2 molecules.

Aqueous-based sorbents also have the potential to increase the total CO_2 absorption by increasing the ratio of CO_2 to amine sites compared to the ratio without H_2O. Hack et al.[7] shows mechanisms for CO_2 adsorption with H_2O and without H_2O. Without H_2O, one mechanism shows that one CO_2 molecule requires two secondary amine sites for adsorption. On the other hand, in the mechanism with H_2O, CO_2 forms a bicarbonate ion, which only requires one amine site. The authors proposed similar ratios for primary amine sites.

Aqueous based sorbents can also be effective at controlling humidity. If the H_2O vapor in the gas flow reached its saturation vapor pressure as the flow exited the module, then the RH would be 100% based on the temperature of the liquid. However, the presence of high concentrations of dissolved species will reduce the humidity exiting the module. As described by Raoult's law, the vapor pressure of H_2O in contact with a liquid will be proportional to the mole fraction of H_2O n the liquid. Because high concentrations of amines and buffers will be dissolved in H_2O, its mole fraction will be reduced. Therefore, the RH of the flow exiting the module will likely be lower than 100% RH. However, it will be characterized in the Phase I work.

B. Characterize Sorbent Performance in Small Scale Hollow Fiber

For this project, Reaction Systems' automated testing apparatus that was used for solid sorbent testing was modified to accommodate tests using a flowing liquid sorbent. A schematic of the test apparatus is shown in Figure 2. The gas handling manifold that was fabricated for the RCA sorbent tests was designed to produce CO_2 partial pressures that are expected in an EVA application, and therefore, it did not require significant modification for initial tests. The manifold is equipped with pneumatic on/off valves and mass flow controllers so the flows through each line can be controlled to desired values. Tests can be carried out with mixtures of CO_2 in N_2, whereas a separate supply of N_2 flows through a temperature-controlled H_2O saturator to produce the desired relative humidity levels after the flow is recombined with the CO_2 and N_2 mixture. A Vaisala RH sensor can be attached to the feed line to measure RH going into the module and confirm that the desired RH is being generated by controlling the flow through the saturator. The RH sensor was also moved to the line exiting the module (as shown in the figure) to measure the RH exiting the module. The system also includes a by-pass line so that the conditions in the feed flow can be set and monitored prior to it being directed through the module.

The primary modification to the previous system was made where the mixed and humidified feed flow enters the test section. In the unmodified test rig, the flow entered a packed bed filled with solid sorbent beads and then the flow was directed into a CO_2 NDIR analyzer. For these tests, the packed bed was replaced with fittings to allow the installation of the HFM's. In these tests, the process flow was directed through the lumen side (flow inside the individual hollow fibers) of the module. Initial tests were carried out where the CO_2 partial pressure was varied, while the liquid flow rate was maintained at a constant value and then at a constant gas flow rate while the liquid flow rate is varied. Typical gas flow rates were on the order of 100 sccm up to 1500 sccm. The higher flow rates produced residence times representative of those existent in a full scale system, and this is discussed further in later sections of this paper. The flow exiting the module was directed into a California Analytical CO_2 NDIR analyzer for analysis of the CO_2 concentration exiting the contactor.

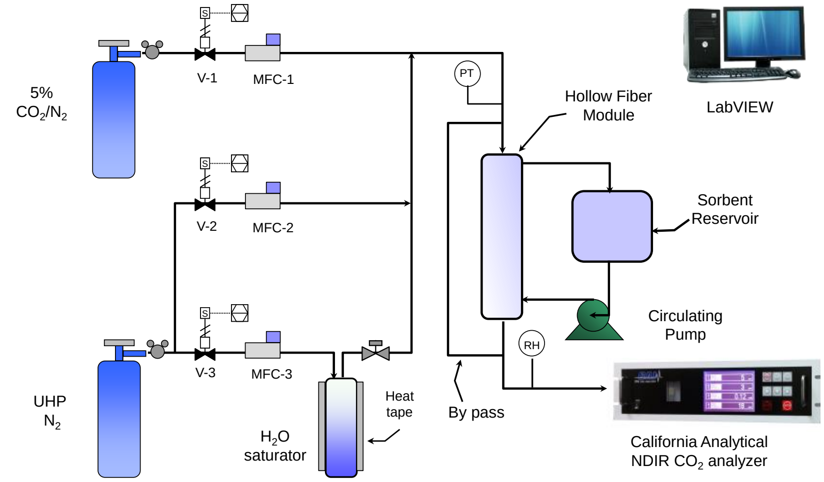


Figure 2. Reaction Systems' test apparatus.

The liquid sorbent was contained in a 2.5-gallon reservoir and was pumped through the shell side of the module using a Stenner model S3002 peristaltic pump. This pump has a range between 10 and 45 ml/minute; initial tests were carried out at a flow rates from 15 to 44 ml/min. In the current configuration, the liquid is flowing from bottom to top, whereas the process flow goes from top to bottom, and therefore tests are being carried out in a counter current mode. However, in the initial tests with amine-based sorbents, the liquid flow is maintained at a rate that provides a large excess sorbent capacity and therefore there will be very little change in the sorbent CO_2 concentration as it passes through the shell side. As a result, the relative flow directions had little effect on the experimental results. The overall sorbent loadings were calculated using the differences between calculated CO_2 and H_2O concentrations entering the module and the measured concentrations exiting the unit. A pressure transducer mounted on the entrance line of the process flow was used to calculate the pressure drop on the gas side of the module assuming that the pressure of the process flow is ambient after it exits the module.

Reaction Systems procured hollow fiber modules from commercial sources. Three hollow fiber modules were purchased from 3M Liqui-Cell. The modules include a 1-in diameter x 5.5-in length MM series membrane, a 1.7-in diameter x 8.75-in length MM series membrane, and a 2.5-in diameter x 8-in length EXF series membrane. In all three cases, the fibers are made from X50 polypropylene.

Although total surface areas are not included in the specifications, a recent paper cited a surface area of 1.4 m^2 for a 2.5-in diameter by 8-in length Liqui-Cell module. Therefore, the module has a surface area to volume ratio of 60 m^2/ft^3 or 21.2cm^2/cm^3. Using this value, estimates of the surface areas for these modules are 0.15 m^2, 0.71m^2, and 1.4 m^2, for the 1 inch (2.54 cm) diameter, 1.7 inch (4.32 cm) diameter and 2.5 inch (6.35 cm) diameter modules, respectively.

Similar test procedures used for characterization of solid sorbents prior to the apparatus modifications previously described were used to characterize the HFM/sorbent performances. Once the candidate solution was prepared, it was transferred into the reservoir. The pump was then activated which circulated the sorbent solution through the shell side of the HFM. In all but the initial tests with H_2O as the sorbent, the flow was maintained at 44 ml/min, the maximum flow of the pump. At this point, the CO_2 and nitrogen flows were set to establish conditions desired for the first set point as the flow was directed through the bypass line. When the readings from the CO_2 analyzer and the RH sensor were stable and consisted with the desired test conditions, the flow was then directed through the HFM. For the majority of tests, each test condition was maintained for approximately 20 minutes or until the CO_2 concentration and the RH values were stable. At that point, the conditions were changed to the next set point; this process was repeated until all test conditions were met. After the data was obtained at the final test condition, the flow was switched back to the bypass to verify that the CO_2 and RH values agreed with the desired tests conditions. Since the CO_2 concentrations generally progressed from low to high over the course of the test, obtaining by-pass values at the start and end of each test provided a good assurance that the CO_2 concentrations entering the module were accurate at all test conditions.

Extended duration tests were also conducted where conditions were held at a single condition for a longer period of time. These tests were conducted in order to measure the total CO_2 weight capacity as well as the weight capacity prior to the outlet concentration reaching the maximum allowable module outlet concentration of 3.0 mm Hg. In these tests, the single setpoint was maintained until the outlet concentration reached 2.5 mm Hg, or until it reached the subjected inlet concentration and the sorbent was at full capacity, which was approximately 1400 minutes in certain tests. The same bypass utilization procedure was conducted before and after these tests, as well.

III. Results

A. Extended Breakthrough Tests

As pointed out previously, the quantity of sorbent needed to control the CO_2 produced in an EVA is an important parameter. Therefore, a test to measure the CO_2 uptake with a solution consisting of 50% amine-based sorbent 1 (ABS-1)/ 50% H_2O was carried out. This test provided information on the ultimate capacity of the ABS-1 / H_2O mixture as well as the uptake efficiency and the ability of the system to maintain the outlet CO_2 concentration below 2.5 mm Hg CO_2 partial pressure. The test was conducted with the 1- inch diameter, 4.32 in^3 volume, 3M Liqui-Cel hollow fiber module. The total gas flow rate was 715 sccm with a CO_2 partial pressure of 13.5 mm Hg and nitrogen balance. The ABS-1 / H_2O mixture was circulated through the shell side of the module at a flow rate of 44 mL / min and the total quantity of the liquid mixture contained within the reservoir and system lines was 45 mL, or 45 g. The results of the test are depicted in Figure 3. The system maintained the outlet CO_2 partial pressure below 2.5 mm Hg, or 0.41% for a total of 650 minutes. At this point during the test, the total weight loading was 38.8%. After 1400 minutes, the figure shows that the sorbent was effectively saturated and was absorbing relatively low concentrations of CO_2. At this point, the CO_2 loading was 53%.

The data collected can be used to estimate the amount of sorbent that would be needed assuming that it can be fully regenerated. Previously, it was shown that the total CO_2 produced in an EVA is 650 grams. At a loading of 38 wt%, then the amount of sorbent required is 1060 grams. The density of this material is 1.0 g / mL, and therefore, the total volume required is 0.037 ft^3.

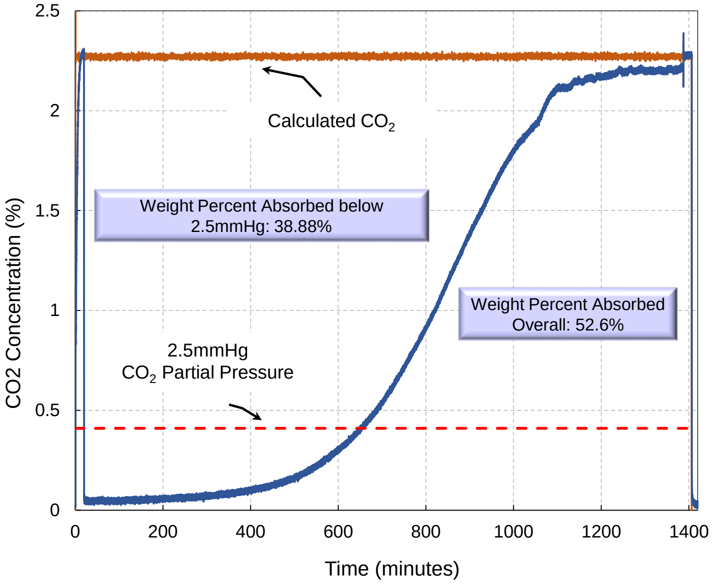


Figure 3. CO_2 uptake results for extended breakthrough test.

B. Tests Carried out with ABS-1 and H_2O

Tests were carried out with a liquid sorbent that consisted of 50% ABS-1 and 50% distilled H_2O . The results of these tests are shown in Figure 4.

In the first test with the amine-based sorbent, which is shown in Figure 4, the CO_2 partial pressure was set to 9.15 mm Hg at a total flow of 110 sccm. The liquid inventory was 200 ml, and it was circulated through the module at flow rates ranging from 40 ml/min to 15 ml/min. The results show that when the flow was directed through the bypass the measured and calculated CO_2 concentrations were equal. However, when the process flow was switched to the module and the sorbent flow was set to 40 ml/min, the CO_2 concentration exiting the module decreased immediately to 0.02%, which is equivalent to a CO_2 partial pressure of 0.15 mm Hg. This value is well below the allowable limit of 3.0 mm Hg set for this system. In addition, and unlike the tests with H_2O shown previously, the CO_2 level did not change when the sorbent circulation rate was decreased to 22 ml/min and 15 ml/min.

Overall, the two tests with the ABS-1 sorbent were very encouraging and demonstrated the potential of this approach to control CO_2 levels in the suit for recovery after the mission is complete. The next series of tests were conducted at more representative conditions in order to collect data that can be used to size a full size unit that would be needed in a spacesuit.

C. Tests at Representative Conditions

After demonstrating that CO_2 could be removed with the hollow fiber module from a flow of 110 sccm using the 50% ABS-1/50% H_2O sorbent mixture, tests were then carried out at higher flow rates and partial pressures that are more consistent with the conditions in an application. One way to conduct tests under realistic condition is to use existing data to correlate inlet partial pressure to metabolic rate. Recent work by Meginnis et al.[8] contains data showing the cyclic CO_2 partial pressure at the metabolic rates specified in the “Max Transient PLSS Profile”. The metabolic rates in the profile were also included in the paper and therefore the average inlet CO_2 partial pressure can be used to estimate a corresponding metabolic rate.

Another measure of metabolic rate is the rate of CO_2 injection. Several efforts have been carried out to challenge various RCA builds with CO_2 and they have correlated CO_2 injection rate with metabolic rate. The data from Papale et al.[9] were used to generate a plot of CO_2 injection rates as a function of metabolic rate for a full-scale system. These values were then scaled down for the 4.3 in^3 module size assuming the full scale injection rate corresponds to the full scale size requirement of 0.231 ft^3 less the sorbent volume allocation of 0.037 cf previously discussed.

Plots of metabolic rate versus CO_2 partial pressure and scaled CO_2 injection rate as a function of metabolic rate are presented in Figure 5. As shown in both cases, there is a linear relationship and the equations of best fit lines, shown in both charts, were used to calculate metabolic rate and the scaled injection rates of CO_2. These relationships were used to calculate metabolic rate as a function of CO_2 partial pressure in the tests carried out under representative conditions.

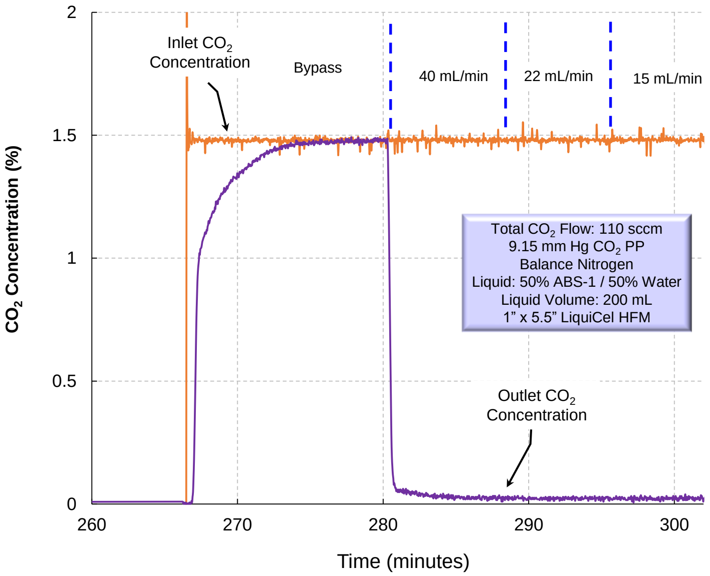
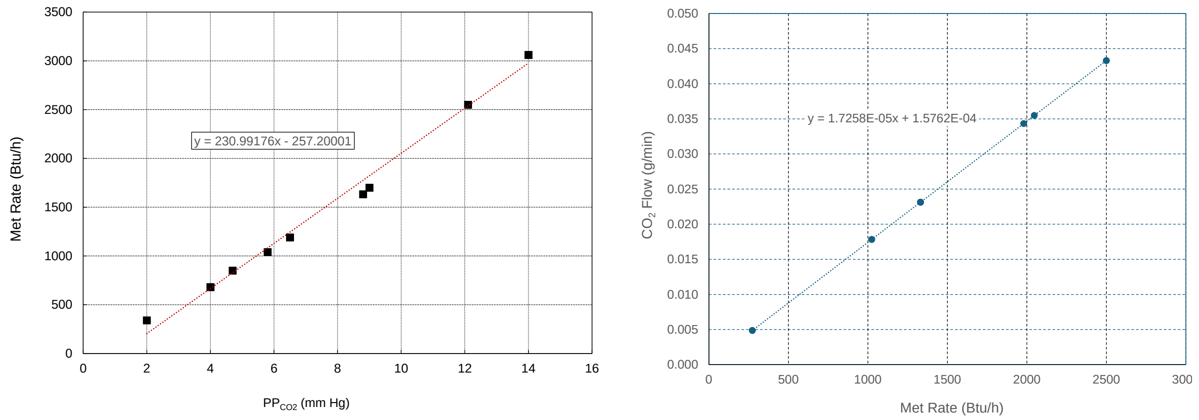


Figure 4. CO_2 uptake results with 50% ABS-1 / 50% H_2O.

While there is a good correlation between metabolic rate and PP_{CO2} in the tests reported by Meginnis et al.[8], simply matching CO_2 partial pressures in the tests with the HFM is not sufficient to set a realistic test condition because matching the PP_{CO2} at a very low total flow is a different test condition than matching the PP_{CO2} at a very high total flow. Therefore, PP_{CO2} can be used to estimate metabolic rate if the total flow is consistent with that needed in a full scale system. The residence time depends on total flow and module size. The maximum allowable volume for the system is 0.231 ft^3, which is comprised primarily of the sorbent volume and the module. The volume of sorbent required from the CO_2 loading, discussed in Section A, is 0.037 ft^3. Therefore, the allowable module size is 0.194 ft. With ventilation loop flows between 4 and 6 acfm, the range of residence times that would be representative for a full scale system is 0.03 to 0.05 minutes.

Tests under more representative conditions were first carried out with a solution consisting of 50 wt% ABS-1 and 50% H_2O using the 1-in diameter, 4.3 in^3 HFM. This mixture was chosen to reduce the solution viscosity in the initial tests and also to take advantage of any absorptive capacity that H_2O can have as shown in Rxns 2 and 3. Tests



Based on data from Meginnis et al. ICES-2017-105

Based on data from Papale et al ICES-2014-196

Figure 5. a) Metabolic rate as a function of PP_{CO2} based on the data from Meginnis et al. (left); b) CO_2 injection rate scaled to the 4.3 in^3 module size as a function of metabolic rate (right).

were conducted at CO_2 partial pressures of 13.8 mm Hg, 8.4 mm Hg, and 7.84 mm Hg. The CO_2 flow rates at the first two conditions were 0.027 g/min, whereas the flow rate at the last condition was 0.036 g/min. In each case the CO_2 was mixed with nitrogen, the total flow was maintained, and no moisture was contained in the feed mixture. The liquid sorbent was circulated through the shell side of the HFM at a rate of 44 cc/min.

The results of this test are shown in Figure 6. For the first 20 minutes of the test, the total flow was 700 sccm and the CO_2 concentration was set to 2.29% and the flow was directed through the module bypass. As shown, the concentration of the CO_2 exiting the module increased and reached the inlet concentration. At a time of 19.7 minutes, the gas flow was directed through the lumen side of the HFM, and the figure shows that the CO_2 concentration dropped rapidly to a value of 0.07 vol%, which is well below the value of 0.4%, which is equivalent to 2.5 mm Hg at ambient pressure in Colorado. Under these conditions, the partial pressure entering the module was 13.8 mm Hg and the residence time was 0.10 minutes, somewhat higher than the values listed in the previous section. After 20 minutes at this condition, the nitrogen flow was raised, resulting in a CO_2 concentration of 1.4%, a decrease in PP_{CO2} to 8.4 mm Hg, and a drop in residence time to 0.060 minutes, which is much closer to the required residence time range outlined in the previous section. Under these conditions the CO_2 concentration exiting the module rose slightly to 0.09%, again, well below the limit of 0.4 %. Finally, for the third set point, the nitrogen flow was raised again and the CO_2 flow was raised to 0.036 g/min, increasing the inlet CO_2 concentration to 1.3% and the residence time to 0.042 min, which is in the range of 0.03 to 0.05 minutes, outlined in the previous section. At this set point, the CO_2 concentration exiting the module is 0.17%, still well below the limit corresponding to 2.5 mm Hg.

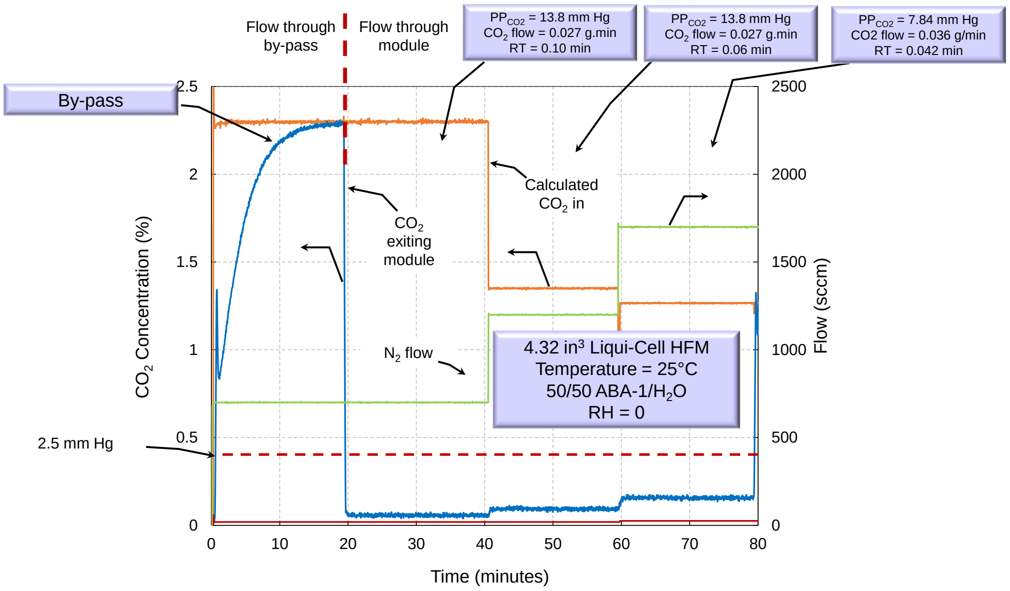


Figure 6. Performance of the 4.3 in^3 HFM at representative conditions with a sorbent consisting of 50% ABS-1 and 50% H_2O in a dry feed.

Overall, these are very encouraging results and demonstrate the concept that CO_2 levels can be controlled to less than 2.5 mm Hg at representative flow rates with a HFM that is circulating a solution of H_2O and ABS-1. Moreover, the CO_2 flow rate at the last set point was 0.036 g/min. This value is very close to the value of 0.041 g/min, which is equivalent to the maximum CO_2 production rate of 3.2 g/min, scaled to the 4.3 in^3 module size. Finally, the residence time at that set point was 0.042 minutes which is also consistent with the target residence time identified in the previous section. However, these tests were done without adding humidity and therefore a test to measure the module performance with humidity added to the feed mixture was then carried out.

A test was also carried out with 20% RH added to the feed mixture and the data obtained were similar to the results in the previous figure. Three different set points were used, resulting in CO_2 concentrations of 1.9%, 1.1%, and 1.0% and corresponding PP_{CO2} values of 11.47, 6.71, and 6.51 mm Hg. The RH was maintained at 20% and the addition of the humidified flow resulted in residence times of 0.083 min, 0.048 min, and 0.034 min, which are somewhat lower than those shown in the previous figure. Once again, the CO_2 values exiting the module are all well below the 0.4% limit and are stable at each set point. In this test CO_2 concentrations of 0.06%, 0.07%, and 0.12% were measured exiting the module and these values are lower than those measured in the previous tests at similar test conditions. These results are also very encouraging and show that the addition of humidity does not have an adverse effect on performance and may even have a positive effect of the HFM performance.

In the previous tests, the RH was measured in the inlet manifold but was not measured in the exit flow. In the next tests with the 50%ABS-1/50% H_2O solution, the RH sensor was placed on the exit line to measure what effect the solution was having on the RH in the outlet process flow.

This test was then carried out under similar conditions as the previous tests. At all test conditions the RH entering the module was maintained at 20% and the CO_2 concentrations exiting the module were similar to those in the previous figures, and all are well under the limit of 0.4% as would be expected. However, the RH exiting the module was close to 100%, which means that rather than removing humidity from the process flow, the amine solution is adding moisture, which is not an acceptable condition.

This addition of H_2O is likely due to the high concentration of H_2O in the amine solution, and therefore to reduce the RH exiting the module, a test was carried out where the H_2O concentration in the ABS-1 mixture was reduced to 30% and the concentration of ABS-1 was increased to 70%. The conditions used are similar to those in the previous test, with the exception that the RH added to the feed mixture was raised to 40%. The results of this test are shown in Figure 7 and Figure 8. Figure 7 shows that reducing the concentration of H_2O in the absorbing solution from 50% to 30% had a substantial effect on the RH exiting the module, as the RH has decreased from 98% to 38%. This drop shows that the concentration of H_2O in the absorbing solution does have a very strong effect on the RH in the outlet process flow.

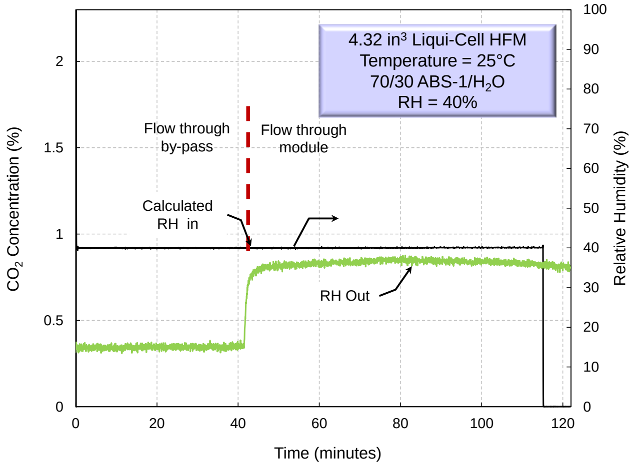


Figure 7. Reduced RH levels exiting the module with 70% ABS-1 and 30% H_2O sorbent.

While the results in Figure 7 are positive and show that RH can be controlled by lowering the H_2O, the absorbing solution, the results in Figure 8 shows that reducing the H_2O concentration also has an adverse effect on the effectiveness of the solution to remove CO_2 . The figure shows that reducing the H_2O concentration results in higher CO_2 concentrations exiting the module at all test conditions. For example, at the first set point at an inlet concentration of 0.42%, the CO_2 concentration exiting the module is 0.29% and therefore the solution is only removing about 31% of the CO_2 flow. Similarly at an inlet concentration of 1.4%, the concentration exiting the module is 1.2%, which results in a percent removal of less than 15% of the inlet CO_2 flow.

A series of tests was carried out to more comprehensively characterize the effects of H_2O concentration of the absorbing solution on CO_2 uptake and RH exiting the module and in all cases, the results agree with those presented in the previous figures. For example, at an inlet PP_{CO2} of 8.69 mm Hg and a solution H_2O content of 40%, the PP_{CO2} exiting the module was 2.6 mm Hg, which is just above 2.5 mm Hg but still well below the upper limit of 3.0 mm Hg. However, when the H_2O concentration was reduced the 20%, the PP_{CO2} exiting the HFM increased to 8 mm Hg, well above the limit. Similar results were obtained in tests conducted at lower PP_{CO2} in the process flow. Moreover, the results demonstrated that higher H_2O content in the solution produced higher RH values in the process flow. For example, with a solution concentration of 20%, the RH was 28%, whereas when the solution H_2O concentration was increased to 40%, the H_2O increased to over 50%.

Overall, these results agree with the data presented in Figure 7 and Figure 8 and show that there is a trade-off between removing CO_2 and humidity. Solutions with a higher H_2O content control CO_2 well but produce high RH values in the process flow, whereas solutions with lower H_2O content can keep humidity low but also have reduced effectiveness in controlling CO_2. Therefore, a method to increase the CO_2 removal performance of lower H_2O content solutions was needed.

3. *Tests with a pH Modifier*

There are multiple suggestions of mechanisms by which gas phase CO_2 absorbs onto primary and secondary amine sites [10]. However, the pathway followed for gas phase CO_2 to be absorbed by a solution of ABS-1 and H_2O is not clear. It likely includes dissolution of CO_2 in H_2O to form carbonic acid and the subsequent dissociation of carbonic acid into H^+ and HCO_3^- ions as shown in Rxns 2 and 3. The absorption could then consist of an interaction of the bicarbonate ion with the amine functions in ABS-1. One factor that could be affecting the absorption is the solution pH.

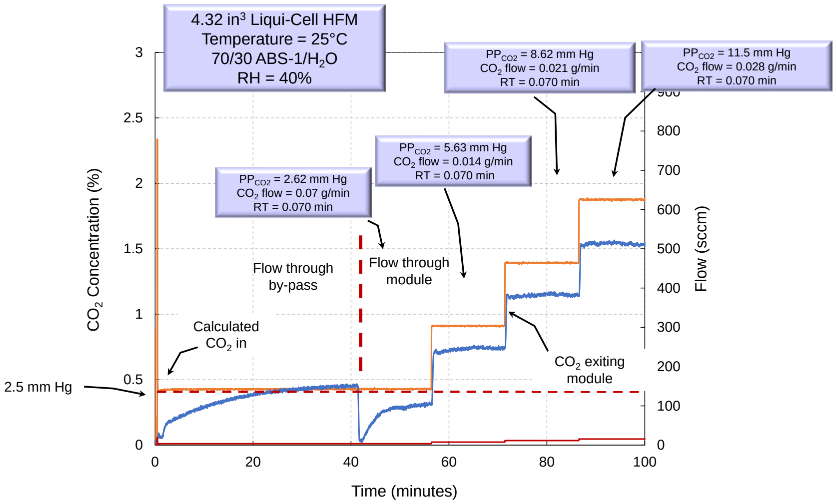


Figure 8. CO_2 levels exiting the module with 70% ABS-1 and 30% H_2O sorbent.

Therefore, the next test was carried out under the same condition used for the tests shown in Figure 7 and Figure 8 with a solution consisting of 70%ABS-1/30% H_2O. However, in this test, the H_2O contained a pH modifier (PHM). The results of the test with the solution modifier are shown in Figure 9. As described before, the test included five different setpoints with varying inlet PP_{CO2} and CO_2 injection rate. According to the metabolic rate and inlet PP_{CO2} relationship established in Figure 5, the metabolic rates of the five conditions were 320 Btu/h, 967 Btu/h, 1618 Btu/h, 2283 Btu/h, and 2884 Btu/h. The metabolic rates as determined by the CO_2 injection rate in Figure 5 are slightly different as a result of the difference in test conditions, and the corresponding rates are 396 Btu/h, 802 Btu/h, 1207 Btu/h, 1613 Btu/h, and 2077 Btu/h. With either correlation, the test condition accounted for a comprehensive metabolic range.

The results in Figure 9 show that there is a substantial improvement in performance as a result of the addition of the PHM. At all of the test conditions, the CO_2 concentrations exiting the HFM are 0.04%, which is a factor of 10 below the limit of 0.4%. This result is significantly lower than the results shown for similar conditions in Figure 8. For example, at the fourth test condition, the inlet PP_{CO2} is 11.0 mm Hg, the residence time is 0.07 min, and as just mentioned, the CO_2 concentration in the process flow is 0.04% or 0.25 mm Hg. On the other hand, in the test carried out without the PHM depicted in Figure 8, the last test point was conducted at a similar set of test conditions of 11.5 mm Hg PP_{CO2} and a residence time of 0.07 min, and the CO_2 concentration coming out of the module was 1.6% or 9.9 mm Hg. This is a factor of four over 2.5 mm Hg. Finally, the CO_2 flow in the last set point was 0.036 g/min, which is very close to the maximum flow required of 3.2 g/min scaled to the 4.3 in^3 module.

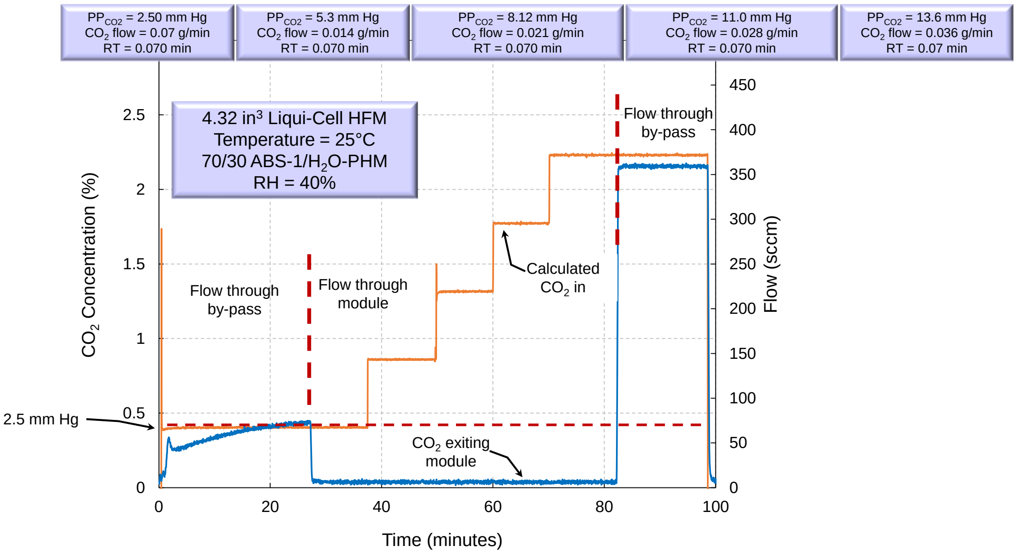


Figure 9. Results of a test at low residence time with a sorbent consisting of 70% ABS-1/30% H_2O.

These tests were carried out under very similar conditions and the only difference between the two is the presence of 0.1 wt% Na_2CO_3 in the H_2O fraction of the sorbent solution. Therefore, the improvement in performance has to be attributed to the salt addition. While the rationale for adding this compound was that it could increase the concentration of bicarbonate anions, the dramatic improvement in performance that was observed would seem to exceed that function. Since the combination of carbonate, bicarbonate and H^+ ions can act as a buffer, the actual function could be at adjusting the pH to a specific value. However, at this point, the reason behind the improvement in performance is not known.

While the CO_2 control was vastly improved by the addition of the PHM, there was little effect on the RH exiting the module. With a feed mixture RH of 40%, the RH exiting the module was 48%, slightly higher than the inlet concentration. This shows that solutions with lower H_2O concentrations are needed and the improvement in performance with PHM could result in good control of both CO_2 and H_2O.

Tests were then carried out with a solution consisting of 90% ABS-1/10% H_2O. The CO_2 inlet conditions were similar to those in the previous two tests, concentrations ranging from 0.4% up to 1.7%, corresponding to PP_{CO2} from 2.4 mm Hg up to 10.7 mm Hg and total flows through the module resulting in the same residence time of 0.07 min. In this case, the CO_2 values were somewhat higher than those observed in Figure 9, with the 30%ABS-1/70% H_2O solution. However, they are lower than those obtained in the 30%ABS-1/70% H_2O without PHM, shown in Figure 8. For example, at a concentration of 1.28% which corresponds to a PP_{CO2} of 8.0 mm Hg, the concentration exiting the module is 0.32%, below the limit of 0.4%. In the test of the 70%ABS-1/30% H_2O without PHM, at the concentration of 1.4%, the CO_2 concentration exiting the module was 1.17% well above the limit of 0.4% and a factor of close to four higher than the results with Na_2CO_3. However, at the highest inlet CO_2 concentration the CO_2 concentration in flow exiting the module was 0.8% which is above the limit and therefore the 90% ABS-1/10% H_2O mixture does not meet the requirements for CO_2 control. On the other hand, reducing the H_2O concentration to 10% has had a dramatic positive effect on the RH exiting the module as it has decreased from 48% to 20%. These results provide more evidence that the RH exiting the module is strongly dependent on the concentration of H_2O in the sorbent mixture.

A test was then carried out with a sorbent that contained 80%ABS-1/20% H_2O, with the PHM. The conditions used in this test were similar to those used in the recent tests and the results are shown in Figure 10. Once again, CO_2 concentrations used ranged from a low of 0.35% up to 1.9%, which correspond to CO_2 partial pressures of 2.2 mm Hg to 12.0 mm Hg, respectively. The same total flows were used in this test resulting in a residence time of 0.07 min for all conditions. The figure shows that in this case, the CO_2 concentrations are all well below the limit of 0.4%, even at the highest partial pressure. The figure also shows that the RH exiting the module is about 32%, which is lower than the 40% value which is being injected into the module.

Overall, these results are very positive and show that a sorbent mixture has been identified that can maintain CO_2 concentrations at below 2.5 mm Hg and still produces acceptable RH levels. Although the data here show that the CO_2 was maintained at acceptable levels, it was increasing at the last set point, and therefore additional tests were carried out with a solution containing a higher concentration of H_2O and at shorter residence times.

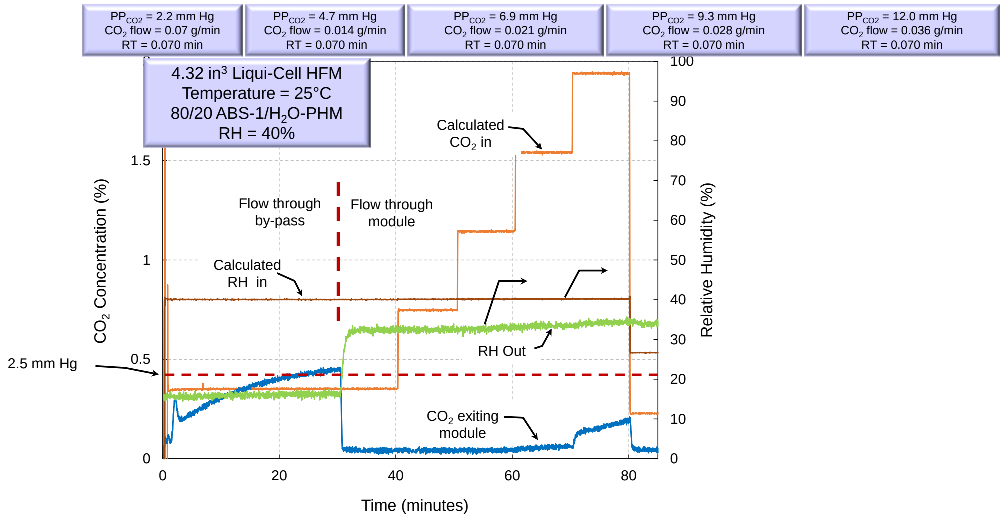


Figure 10. Test results with a sorbent consisting of 80% ABS-1/20% H_2O.

Figure 11 shows the results obtained with a solution containing 70%ABS-1/30%H_2O at higher overall flows which results in a lower residence time of 0.047 min. The CO_2 concentrations used ranged from 0.29% up to 1.6% which corresponds to PP_{CO2} from 1.8 mm Hg up to 10.2 mm Hg. In these tests, the total flow rate was maintained at 1500 sccm which results in a residence time of 0.047 minutes and is in line with the required residence time discussed earlier. In addition, the CO_2 flow rate at the final set point was

0.036 g/min which is very close to the maximum required value of 3.2 g/min scaled to the module size of 4.3 in^3. The metabolic rates corresponding to the inlet partial pressure correlation from Figure 5, were 159 Btu/h, 643 Btu/h, 1129 Btu/h, 1613 Btu/h, and 2099 Btu/h. The metabolic rate as determined by the CO_2 injection rate in Figure 5 were essentially equivalent as a result of the adjusted residence time; they were 396 Btu/h, 802 Btu/h, 1207 Btu/h, 1613 Btu/h, and 2077 Btu/h. For all of the conditions tested, Figure 11 shows that the CO_2 concentrations exiting the module are all very low at 0.07% and the levels do not increase at the highest PP_{CO2}.

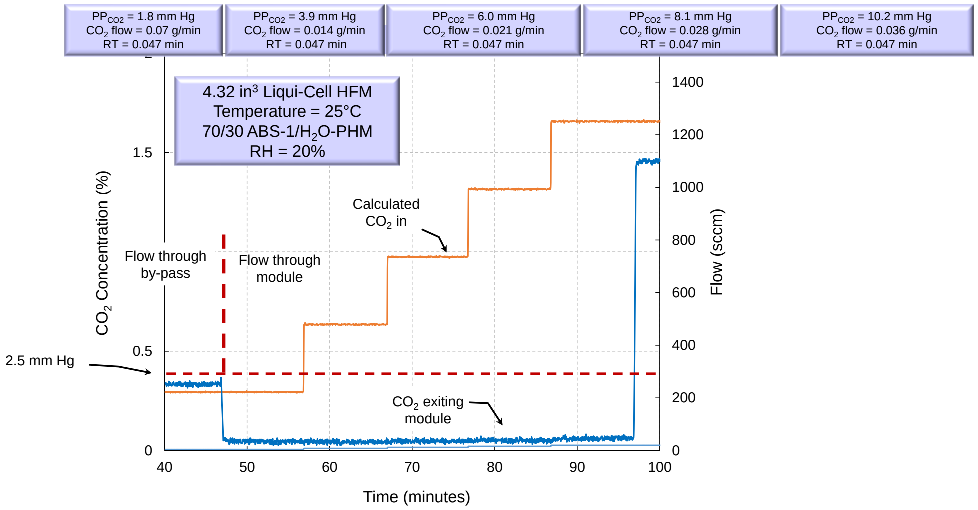


Figure 11. Results of a test at low residence time with a sorbent consisting of 70% ABS-1/30% H_2O.

Once again, these are very positive and encouraging results. They show that this process has the potential to be a very effective method to control CO_2. The data have shown that solutions containing 70%ABS-1/30% H_2O are very effective for CO_2 but have somewhat higher than desired RH values exiting the module. On the other hand, solutions containing 80% ABS-1/ 20% H_2O are more effective at reducing humidity but are not as effective for CO_2. It is likely that solutions with H_2O concentrations between these values would provide better performance.

D. Initial Thermal Regeneration Results

One important parameter for a sorbent to be used in this application is its ability to be regenerated so that the CO_2 and H_2O can be recovered. Several tests have been carried out to measure the working capacity of ABS-1. A series of tests were run where a solution of 60% ABS-1 and 40% H_2O was exposed to a flow of 1.5% CO_2 at a flow rate of 1200 sccm, which results in a residence time of 0.06 min, which is near the representative values that will be required for a full scale unit. After the sorbent was saturated with CO_2 it was removed from the reservoir and placed in a round bottom flask and connected to a roto vap that reduced the pressure to less than 0.1 atm. The flask was immersed in a H_2O bath that was initially maintained at ambient temperature for 5 hours and then the temperature was raised slowly to a maximum value of 48°C. This level of vacuum and temperature is well below the conditions needed for H_2O to boil. During most of the time on the rotovap, small bubbles could be seen evolving slowly from the liquid. After 16 hours under these conditions, the solution lost 33.5 grams which represents 21 % of the total weight of solution. The liquid was then placed in the test rig and exposed to similar test conditions.

The results of these two runs are shown in Figure 12. The results show that in the initial test, at representative flow rates, the module controlled the CO_2 concentration to less than 0.4% (less than 2.5 mm Hg) for over 460 minutes. The test was concluded when the CO_2 concentration reached 0.9%, showing that it was becoming saturated with CO_2. The uptake curve following regeneration is shown on the right side of the figure. It shows that the CO_2 concentration was maintained below 2.5 mm Hg for approximately 260 minutes of runtime. While this isn't as long as the original 460 minutes of run time maintained below the maximum limit in the first run, these results show that the regeneration step had a significant effect on the performance of the sorbent and demonstrate the reusable capability of it. The Phase ll Statement of Work outlines the investigation of improved and more comprehensive regeneration methods.

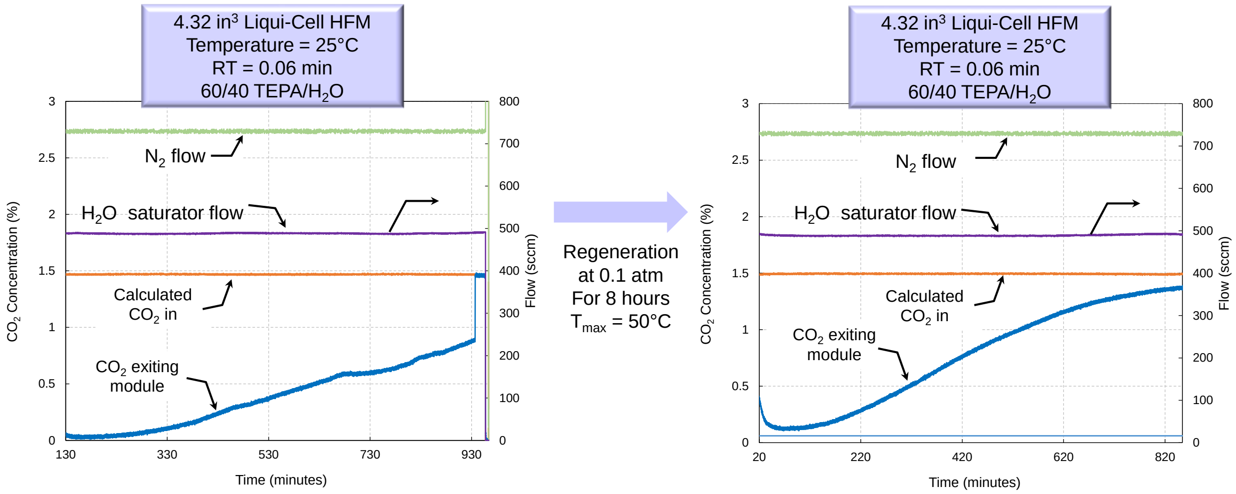


Figure 12. Initial CO_2 uptake test (left) and CO_2 uptake test after regeneration (right).

IV. Summary and Conclusions

In this SBIR Phase I project, Reaction Systems developed a novel system which utilizes a high-capacity liquid sorbent and a hollow fiber module to control CO_2 and H_2O in EVA missions that will accommodate extended mission times and allow for the reclamation of both removed products. Test results obtained in the project show that this approach is very promising and that the liquid sorbents identified have a higher capacity for CO_2 compared to the silver oxide used in the METOX. In addition, tests carried out under realistic conditions show that the system can maintain CO_2 levels well below the required 3.0 mm Hg limit even at the higher metabolic rates.

Tests were carried out with sorbents consisting of mixtures of ABS-1, H_2O, and small amounts of Na_2CO_3. It was found that the percentage of H_2O in the solution strongly influenced the sorbents capacity for both CO_2 and humidity control. Sorbents consisting of a 50/50 mixture of ABS-1 and H_2O were very effective at removing CO_2 rapidly but left very high RH values in the process stream. Reducing the percentage of H_2O to 30% reduced the RH in the flow exiting the module but had an adverse effect on the ability of the module to control CO_2. However, test results showed that adding 0.1 wt% Na2CO3 to the H_2O phase prior to mixing with ABS-1 produced a substantial improvement in the rate of CO_2 absorption.

A sorbent with the composition of 70% ABS-1 / 30% H_2O / 0.1% Na_2CO_3 used in conjunction with a HFM consisting of polypropylene hollow fibers was challenged with an inlet CO_2 flow rate representative of a metabolic rate of 2000 Btu / hr and residence time representative of full scale conditions. It maintained the outlet CO_2 concentration at a constant value of 0.05%, or 0.31 mm Hg, which is significantly lower than the required level of 3.0 mm Hg. In addition, similar liquid sorbent compositions were able to maintain the outlet humidity content of the process stream at 40% RH when challenged with inlet humidity ranging from 40%-90% RH.

While the results of this project are encouraging, additional work is needed to advance the TRL of this technology. Tasks that would be needed include scaling up the module size and operating it in a closed loop test rig, characterizing any trace contaminants that might be included in the process flow, and carrying out multiple adsorption and desorption cycles on the candidate sorbents.

V. Acknowledgments

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